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TREATMENT AND RECOVERY OF FLUORIDE INDUSTRIAL WASTES

Christian J. Staebler, Jr.

Grumman Aerospace Corporation

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16. Abstract

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Pilot studies of centrifugal techniques to separate lime-precipitated bridges from titanium chemical milling, titanium descaling and aluminum deoxidizing solutions show that lime precipitation can give final effluents having fluoride concentrations less than three parts per million. Aluminum conversion coating solutions, however, require secondary treatment with aluminum sulfate to give final effluents having fluoride concentrations less than three parts per million.

Chemical and mechanical property tests show that it is potentially feasible to use calcium fluoride sludge as a strength-maintaining additive for concrete. The reuse of treated rinse waters, the economics of precipitation, and production plans for chemical processing solutions and rinse waters are also presented. (EPA)

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March 1974

TREATMENT AND RECOVERY OF FLUORIDE INDUSTRIAL WASTES

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Program Element 1BB036

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ABSTRACT

This report presents the development and successful demonstration of laboratory and pilot-scale fluoride treatment techniques for selected aerospace and metal-working industry chemical processing solutions and rinse waters. It includes laboratory-scale, lime treatment parameters for chemical processing solutions such as temperature, retention time, pH, slurry concentration and fluoride influent and effluent levels, and ion-exchange treatment techniques to reduce the fluoride concentration of rinse waters to levels less than three parts per million.

Pilot studies of centrifugal techniques to separate lime-precipitated sludges from titanium chemical milling, titanium descaling and aluminum deoxidizing solutions show that lime precipitation can give final effluents having fluoride concentrations less than three parts per million. Aluminum conversion coating solutions, however, require secondary treatment with aluminum sulfate to give final effluents having fluoride concentrations less than three parts per million.

Chemical and mechanical property tests show that it is potentially feasible to use calcium fluoride sludge as a strength-maintaining additive for concrete. The reuse of treated rinse waters, the economics of precipitation, and production plans for chemical processing solutions and rinse waters are also presented.

This report was submitted in fulfillment of Project S800680 (12070 HGH) under the (partial) sponsorship of the Office of Research and Development, Environmental Protection Agency.

Key Words:

Fluoride Industrial Wastes
Lime Treatment
Ion Exchange
Calcium Fluoride Sludge

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SECTION I

CONCLUSIONS

- **Chemical granular quicklime (CaO) proved to be the most effective low-cost material for fluoride treatment of acid-containing chemical process solutions.**
- **Titanium chemical milling solution (10% by volume hydrofluoric acid) can be treated with chemical granular quicklime to give a final fluoride effluent concentration less than three parts per million if a solids retention time (without stirring) of at least 1.5 hours is used.**
- **Titanium descaling solution (40% nitric acid plus 2% hydrofluoric acid) can be treated with chemical granular quicklime to give a final fluoride effluent concentration less than one part per million.**
- **Aluminum deoxidizer solution (2-6 oz./gal. Amchem 7-17 deoxidizer plus 15-20% nitric acid) can be treated with chemical granular quicklime to give a final fluoride effluent concentration less than one part per million.**
- **Aluminum conversion coating (Alodine 1200) can be treated to give a final fluoride effluent concentration less than three parts per million if primary fluoride treatment with chemical granular quicklime is followed by secondary treatment with aluminum sulfate.**
- **The low fluoride levels obtained on the above chemical process solutions (less than the 7.9-ppm fluoride solubility for calcium fluoride reported in the literature) are probably the result of excess calcium in the effluent, brought about by the large amount of lime required initially to neutralize the acid before fluoride precipitation can take place.**
- **Rohm and Haas Amberlite IRA-400 resin is an efficient ion-exchange material for removal of fluorides from process solution rinse waters. The fluoride concentration in such rinse waters was reduced from 60 parts per million to one part per million.**

- **Alcoa F-1 activated alumina, when used in series with Amberlite IRA 400 resin, is an efficient material for maintaining pH control of rinse waters as well as providing a polishing treatment for further reduction of the fluoride content in the waste discharge.**
- **Pilot studies on centrifugal separation and removal of precipitated calcium fluoride sludge using a Sharples Mark III centrifuge provided the data necessary for specification of production equipment and showed the viability of centrifugal separation.**
- **Compression and flexural strength tests showed the feasibility of adding calcium fluoride sludge to concrete to establish sludge re-use capability while maintaining strength levels.**
- **Continuous recirculation of water over concrete made with calcium fluoride sludge showed that an insignificant amount of fluoride leached out of the concrete. This should not present any potential fluoride pollution problems as a result of runoff and infiltration of rainwater into the ground.**
- **An economic evaluation of the chemical costs for the process solutions evaluated showed that fluoride removal would cost between 0.39 and 2.34 cents per gallon.**
- **Based on rinse water ion-exchange effluent results for fluoride, pH and conductivity, treated rinse water can be reused as rinse or process solution make-up water, or disposed of in recharge basins.**
- **Data generated in the studies to remove fluorides from process solutions and rinse waters made it possible to prepare production scale-up plans.**
- **Prototype lime treatment system studies showed that centrifugal separation can remove 95 to 97 percent of the solids generated in the treated 10 percent hydrofluoric acid, titanium chemical milling solution (initial concentration of 177,500 ppm). Settling of the centrate provides a clear effluent with 99.99 percent of the solids removed.**
- **The estimated capital investment of a complete lime treatment system which would include automated lime slaking equipment with a capacity of 500 tons per year, a 20 to 30-gpm centrifuge and a 10,000-gallon settling tank would be $60,000.**

SECTION II

RECOMMENDATIONS

This technology development program strengthened the conviction that further studies are needed to provide the aircraft industry with a total approach to pollution abatement. The following developments are planned under Phase II of this program:

- Although the data established the feasibility of using Rohm and Haas' Amberlite IRA-400 resin in series with Alcoa F-1 activated alumina for fluoride removal from rinse water, the following additional information must be generated before a production-size installation can be set up:
  - Scale up system to pilot size (one cubic foot)
  - Conduct more comprehensive treatment studies on rinse waters generated (including re-use) at metal finishing aircraft facilities using a strong base IRA-400 resin column followed by an activated alumina column. The data obtained would include the fluoride and nitrate removal capacity of the resin, fluoride removal capacity of the activated alumina, effect of flow rate on the performance of the activated alumina, and the fluoride and nitrate concentration in the raw waste, effluent from the resin bed, and effluent from the activated alumina column.
  - Determine if the strong base IRA-400 resin starts to hydrolyze upon repeated cycling, which will be reflected in progressively lower capacity of the resin.
  - Determine if small quantities of heavy-metal cations have any effect on resin upon repeated cycling and establish possible need for cation exchange tower in a production installation.
- Although it was established that chemical process solutions containing fluoride concentrations as high as 100,000 ppm could be reduced to less than three ppm using chemical granular quicklime, a problem still exists,

however, in that some of these solutions also have nitrate concentrations higher than 100,000 ppm. Present New York State standards require that metal processing solutions contain less than 10 ppm of nitrate before being discharged to ground waters. The centrifugal lime precipitation technique will be used in conjunction with a mechanically aided evaporator to provide a comprehensive waste treatment facility capable of removing fluorides, nitrates and chromates. Parameters such as feed rate and steam pressure, and the effect of solution analysis on effluent purity will be established. Once pilot evaporator parameters are established, the economics of nitrate sludge reuse, water recycling and production scale-up will be determined.

- The following information must be established before concrete containing lime treatment sludge can be used for road construction:
  - Maximum amount of sludge that can be added to maintain or increase concrete strength.
  - Short and long-term aging strength through structural testing
  - Long-term leachability, slump, air content, and degree of strength degradation due to environmental exposure.

SECTION III

INTRODUCTION

A steadily increasing number of applications for titanium, super-alloys, and refractory metals in military and commercial products is making it necessary to expand the use of fluoride-containing solutions for cleaning, scale removal and other chemical operations. Mounting public concern about environmental pollution and more stringent government regulations have put increased pressure on metalworking industries and chemical firms that use fluorides, and on those chemical firms that manufacture fluorides to use non-polluting fluoride waste disposal procedures.

The increasing volume of fluoride-containing processing solutions and rinse waters being generated, however, is making existing methods of removing these solutions prohibitively expensive. Most aerospace firms use vendors to dispose of waste solutions. Since vendors may sometimes use questionable treatment and disposal methods, the firms which supplied the waste solutions can be held responsible for vendor-caused pollution damage even though contracts with "hold-harmless clauses" are if effect. Also, since vendors may not normally regenerate fluoride solutions, the fluoride pollution problem may merely be transferred from one location to another. Some waste disposal vendors require that fluoride solutions be completely segregated. This creates storage and handling problems when both large and small processing tanks are being used and when the vendor has tank trucks of only one size. Measures must also be taken to insure the safety of personnel involved in pumping and handling the corrosive and toxic fluoride solutions from user storage facilities to vendor tank trucks.

This project was initiated, therefore, to develop a comprehensive fluoride waste treatment technology for chemical processing solutions and rinse waters used in the aerospace and metalworking industries. The fluoride treatment approach was based on the use of lime precipitation for process solutions and ion-exchange for rinse waters.

SECTION IV

FLUORIDE PRECIPITATION AND CONCENTRATION TECHNIQUES

APPROACH

This phase of the program was directed toward the removal and recovery of fluorides from spent, metal treatment acid solutions and rinse waters in a primary effort to prevent pollution of ground water by discharge of these untreated, fluoride-containing wastes. The treatment approach was based on lime precipitation for process solutions and ion-exchange adsorption techniques for rinse waters.

STUDY AREAS

The task of developing precipitation and ion-exchange adsorption techniques for removal of fluorides consisted of the following technical efforts:

- Chemical analysis of solutions
- Selection of fluoride precipitation materials
- Development of laboratory lime precipitation techniques
- Selection and evaluation of ion-exchange materials
- Development of isotherm data procedures
- Generation of breakthrough data
- Regeneration of Amberlite IRA-400 resin
- Development of a two-stage, ion-exchange system for titanium chemical milling rinse water

CHEMICAL ANALYSIS OF SOLUTIONS

Six fluoride-containing process solutions were chosen for study under this program and analyzed for total fluoride content using the specific ion electrode technique. The typical formulations, uses, and manufacturers for the process solutions studied are shown in Table 1. The total fluoride content (in parts per million) of the solutions is shown in Table 2.

TABLE 1

COMPOSITION AND USES OF FLUORIDE-CONTAINING PROCESSING SOLUTIONS

Fluoride-Containing Process Solutions—Typical Formulations	Typical Uses	Manufacturer
Aluminum Deoxidizer Solution 2-6 oz./gal AMCHEM 7-17 deoxidizer (contains potassium dichromate and fluoride salts) 10-20% volume nitric acid 42° Baume	Cleaning of aluminum parts prior to: • Conversion coating (Alodine) • Masking of parts for chemical milling • Spot welding	AMCHEM Products Inc., Ambler, Pa.
Titanium Descaling Solution 35-45% volume nitric acid 42° Baume Actane #70 1.5-3% by weight or Hydrofluoric acid 1.5-3% by volume, using 70% weight acid.	Cleaning of titanium parts for: • Welding • Removal of heat-treat scale • Painting	Chemical grade acids (sources open) Actane #70 - Enthone Inc., West Haven, Connecticut
Ferrous Alloy Descaling Solution 2-10% volume sulfuric acid. 66°Baume. Sodium nitrate 1-5 oz./gallon. Hydrofluoric acid 1-5% volume. or Actane #70 1-5% by weight Iron (Fe) 4% weight maximum.	Cleaning of ferrous alloys for: • Heat-treat scale removal • Plating	Acids and sodium nitrate (sources open) Actane #70-Enthone Inc., West Haven, Connecticut
Ferrous Alloy Descaling Solution 50% volume nitric acid 42° Baume Hydrofluoric acid 5% by volume, using 70% weight acid	Cleaning of Ferrous alloys for: • Heat-treat scale removal • Plating	Chemical grade acids (sources open)
Titanium Chemical Milling Solution Hydrofluoric acid 10% by volume using 70% acid.	Chemical milling and blanking of titanium parts to effect: • Weight reduction. • Integral stiffening. • Blanked-out parts.	Acid - 70% commercial grade (source open)
Aluminum Conversion Coating Solution (Alodine). Alodine contains chromic acid and complex fluoride salts.	Used to produce a protective coating on aluminum to: • Increase corrosion resistance • Increase paint adhesion	AMCHEM Products, Inc., Ambler, Pa.

TABLE 2

FLUORIDE CONTENT OF CHEMICAL PROCESSING SOLUTIONS

Process Solution	Total Fluoride Content, parts per million
Aluminum Deoxidizing	2,250
Titanium Descaling Solution	60,000
Sulfuric Ferrous Alloy Descaling	16,000
Nitric Ferrous Alloy Descaling	39,600
Titanium Chemical Milling	100,000
Aluminum Conversion Coating	1,750

The fluoride electrode (Figure 1), which is a selective ion electro-chemical sensor designed for use with an expanded-scale pH meter, was selected as an analytical tool because of its simplicity and reliability. Its operation is based on a single-crystal sensing element. The sample solution contacts one face of the crystal and an internal reference solution contacts the other. A standard Calomel electrode is used as a reference electrode. The fluoride analysis procedure used for all samples is shown in the Appendix.

SELECTION OF FLUORIDE PRECIPITATION MATERIALS

Before starting this program, an extensive literature search was conducted to establish the optimum and most cost-effective fluoride-removal materials. Based on this search, fluoride precipitation with lime to yield the relatively insoluble calcium fluoride was selected as the most feasible and economical approach for primary fluoride removal from processing solutions. The limes shown in Table 3 were selected for the initial laboratory studies.

DEVELOPMENT OF LABORATORY LIME PRECIPITATION TECHNIQUES

The following parameters for lime precipitation of fluorides were established for titanium descaling, titanium chemical milling, nitric ferrous descaling, sulfuric ferrous descaling, aluminum deoxidizing and aluminum conversion coating solutions:

- Lime slurry concentration requirement
- Slaking time (where required)
- Starting and maximum reaction temperature
- Process solution-lime slurry ratio
- Solids retention time
- Treated effluent pH
- Treated effluent fluoride concentration

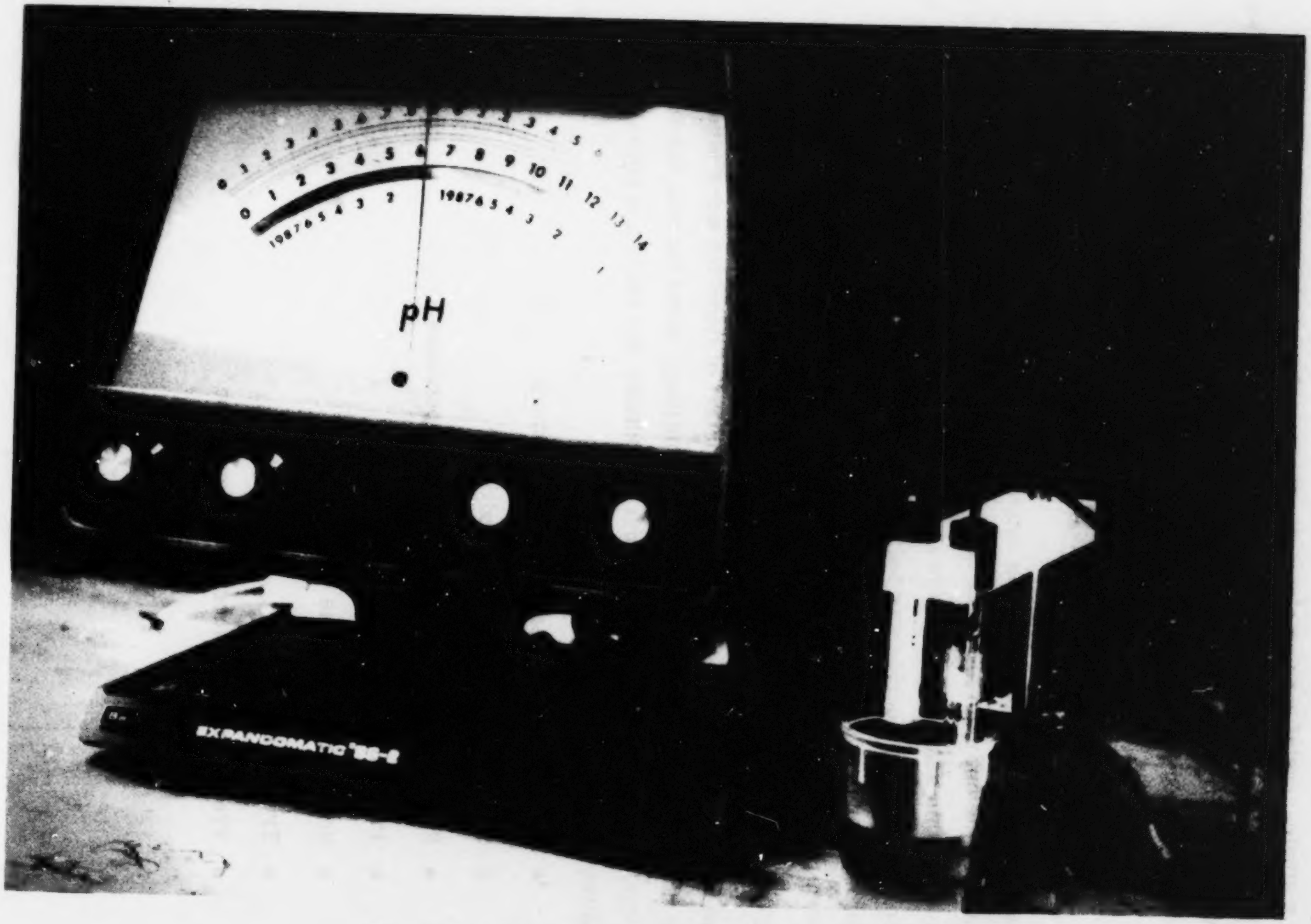
pH
EXPANDOMATIC SS-2

Figure 1. Fluoride Electrode with Expanded-Scale pH Meter

TABLE 3

LIMES USED FOR FLUORIDE PRECIPITATION

Commercial Name	Chemical Composition	Cost Per Ton (dollars)	Bulk Density (lb./cu. ft.)
Chemical Granular Quicklime	CaO	$21.00	68-72
High-Calcium Hydrated Lime	$Ca(OH)_2$	$20.00	20-30
Dolomitic Granular Quicklime	$CaO\text{-}MgO$	$21.50	70-75
Quick Plastic Dolomitic Hydrated Lime	$Ca\,(OH)_2\text{-}$ $Mg\,(OH)_2$	$28.00	30-35
High-Calcium Limestone	$Ca\,CO_3$	$ 7.00	169
Dolomitic Limestone	$Ca\,CO_3\text{-}$ $Mg\,CO_3$	$ 7.00	80-90

High-calcium hydrated lime [$Ca(OH)_2$] was used as a standard to establish the weight of lime required to achieve maximum fluoride removal. The alkali equivalents of the other five limes tested were computed so that the same alkalinity level could be used for subsequent tests. The initial fluoride precipitation tests were conducted on titanium chemical milling solution (10% hydrofluoric acid) and titanium descaling solution (40% nitric acid plus 2% hydrofluoric acid). These two solutions were picked for initial tests, since the titanium chemical milling solution is a weak acid and the descaling solution is a strong acid. The fluoride precipitation results would be indicative of expected results on the other process solutions to be tested. Specific fluoride reduction results achieved for the titanium chemical milling solution and the titanium descaling solution using the six limes tested were as follows.

Titanium Chemical Milling Solution

Lime precipitation data for this test and all subsequent tests were established by treating one-liter volumes of process solution with different lime slurry concentrations. Process solutions and water used to prepare lime slurries were at ambient temperature prior to slaking (where required) and treatment. Lime slurries were mixed by adding the quantity of lime to a measured quantity of water. A 15-ml sample for fluoride analysis was removed from the treated process solution at each indicated retention time. This sample was centrifuged for three minutes in an International Clinical centrifuge and then analyzed.

For the six limes tested, optimum fluoride reduction was achieved with titanium chemical milling solution (10% by volume of hydrofluoric acid) using either chemical granular quicklime or high-calcium hydrated lime (Table 4). The initial fluoride concentration was reduced from 100,000 to 6.45 parts per million. The greatest fluoride reduction occurred at a pH of about 12. It was found that a minimum solids retention time of 60 minutes was necessary with either chemical granular quicklime or high-calcium hydrated lime to achieve maximum fluoride reduction. The heat of neutralization caused a temperature increase of $46^{o}F$-$66^{o}F$, except where high-calcium limestone or dolomitic limestone was used. The limestones produced temperature increases of only $6^{o}F$-$14^{o}F$. The temperature increase due to neutralization occurred within five minutes of lime

TABLE 4

LABORATORY LIME TREATMENT RESULTS FOR TITANIUM CHEMICAL MILLING SOLUTION (10% BY VOLUME HYDROFLUORIC ACID)

Initial Fluoride Concentration (ppm)	Lime Used For Treatment	Slurry Concentration (grams/liter)	Volume Acid: Volume Slurry	Temp. Increase During Neutralization (°F)	Solids Retention Time (minutes)	Effluent Temp. Prior To Solids Separation (°F)	Effluent pH	Effluent Fluoride Concentration, (ppm)
99,500	Chemical Granular Quicklime	178	1:1	46	5 45 60 1140	154 125 105 70	12.2 12.2 12.4 11.7	6.75 - 6.45 6.22
99,500	High-Calcium Hydrated Lime	232	1:1	66	15 30 60 120 240	110 98 86 80 78	12.2 12.2 10.5 12.0 12.0	9.35 9.22 6.74 15.8 10.4
99,500	Dolomitic Granular Quicklime	153	1:1	46 .	10 30 60 180	125 117 100 80	2.9 4.6 7.3 9.7	4,900 740 122 66
99,500	Dolomitic Hydrated Lime	210	1:1	52	10 20 40 60 120 180	115 104 96 90 86 84	6.0 7.0 8.1 8.1 8.1 8.0	202 154 141 133 108 99
99,500	High-Calcium Limestone	268	1:1	6	255	-	2.5	18,600
99,500	Dolomitic Limestone	276	1:1	14	210	-	1.2	30,800

slurry-acid contact. The use of dolomitic limes and limestones was ruled out because the lowest effluent fluoride concentration that could be obtained was 65 parts per million. This was probably due to the fact that the highest pH that could be reached with the dolomitic limes was 3.65 while unreacted lime was still in the beaker. The optimum reductions that were achieved in fluoride content of titanium chemical milling solution with the six limes tested are shown in in Figure 2.

Titanium Descaling Solution

For the six limes tested, optimum fluoride reduction was achieved on titanium descaling solution (40% by volume $HNO_3(42^{\circ}Bé)$/2% by volume HF of 70% weight) using either chemical granular quicklime or high-calcium hydrated lime (Table 5). Chemical granular quicklime and high-calcium hydrated lime at slurry concentrations of 237 and 345 grams per liter reduced total fluoride concentration from 60,000 ppm to 0.615 and 0.297 ppm, respectively. The waste acid-to-slurry volume was 1:1. Maximum fluoride reduction occurred between a pH of 8 and a pH of 10. The low fluoride levels obtained (less than the 7.9 ppm fluoride solubility for calcium fluoride) are probably caused by excess calcium in the effluent resulting from the large amount of lime required to neutralize the nitric acid. Low fluoride levels were also obtained on samples treated with dolomitic granular quicklime (1.36 ppm F^-) and high-calcium limestone (4.79 ppm F^-). The fluoride concentration of samples treated with dolomitic lime, however, rose to 22.6 ppm when solids retention times greater than 10 minutes were used. This was attributed to redissolving of magnesium fluoride. High-calcium limestone may produce an effluent with a fluoride concentration lower than three parts per million, if it is added dry. Liberation of carbon dioxide during neutralization, however, would require control equipment. The optimum reductions in fluoride content of titanium descaling solutions obtained with the six limes tested are shown in Figure 3.

Since optimum fluoride reductions with both the titanium chemical milling solution (10% hydrofluoric acid) and titanium descaling solution (40% nitric acid plus 2% hydrofluoric acid) were obtained using either chemical granular quicklime or high-calcium hydrated lime, these limes were chosen for all subsequent testing. The following results were obtained for ferrous descaling,

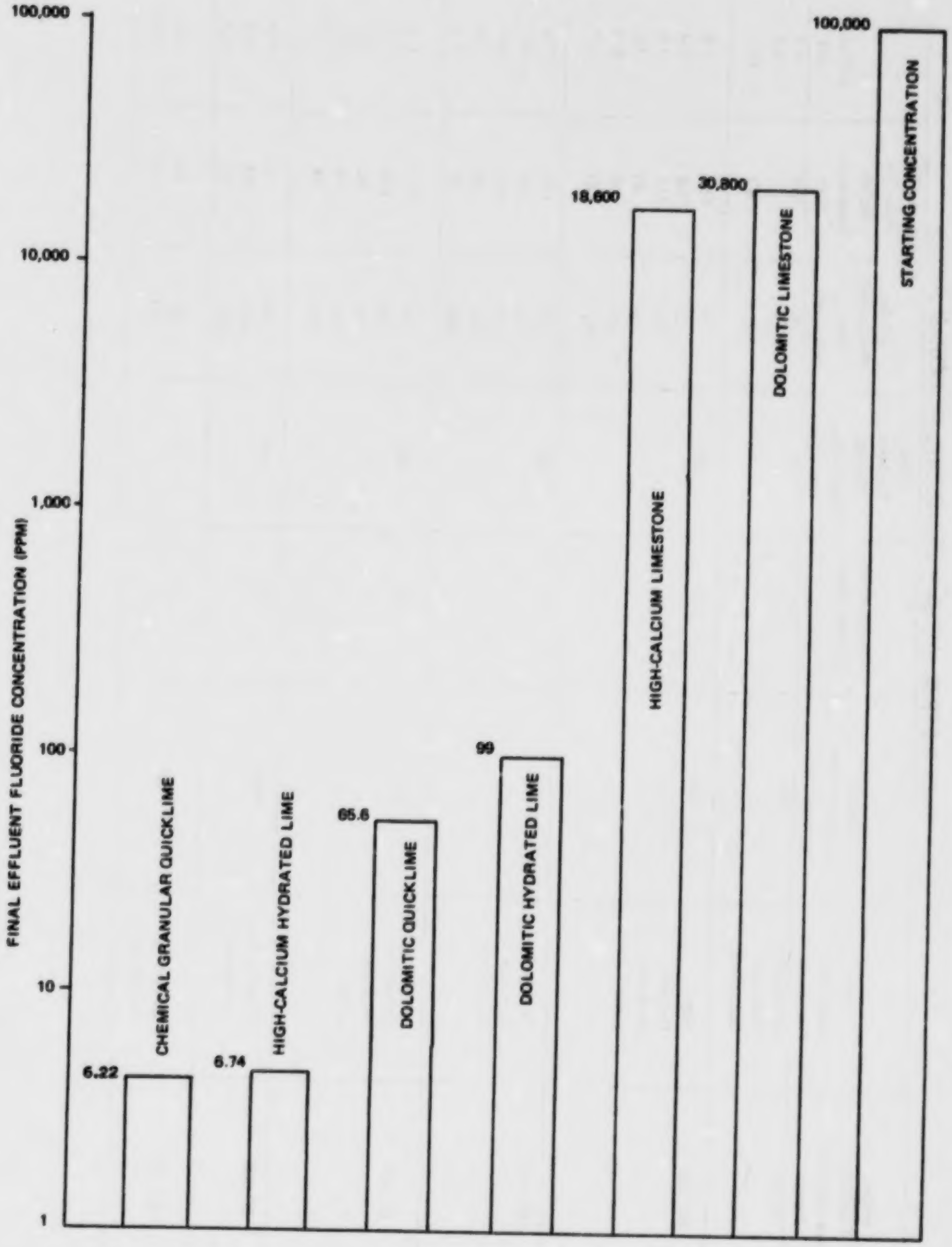

Figure 2. Lime Treatment of 10% by Volume of 70% Weight Hydrofluoric Acid Titanium Chemical Milling Solution

TABLE 5

LABORATORY LIME TREATMENT RESULTS FOR TITANIUM DESCALING SOLUTION

(40% NITRIC ACID + 2% HYDROFLUORIC ACID)

Initial Fluoride Concentration (ppm)	Lime Used For Treatment	Slurry Concentration (grams/liter)	Volume Acid: Volume Slurry	Temp. Increase During Neutralization (°F)	Solids Retention Time (minutes)	Effluent Temp. Prior To Solids Separation (°F)	Effluent pH	Effluent Fluoride Concentration (ppm)
60,000	Chemical Granular Quicklime	237	1:1	94	15	160	4.9	3.46
					30	130	7.9	1.04
					105	92	10.2	0.62
60,000	High Calcium Hydrated Lime	345	1:1	88	5	150	7.6	3.56
					10	136	7.8	0.55
					30	112	7.9	0.30
					60	90	7.8	1.44
					180	78	8.0	0.71
					240	78	7.8	0.40
60,000	Dolomitic Granular Quicklime	225	1:1	104	10	132	5.9	1.4
					30	115	6.2	5.9
					60	100	6.8	13.8
					180	80	7.2	12.4
					240	80	6.4	22.6
60,000	Dolomitic Hydrated Lime	312	1:1	94	10	132	6.8	33.7
					30	106	7.2	18.9
					60	86	7.5	66.0
					135	76	7.2	24.4
					255	74	7.7	34.4
60,000	High-Calcium Limestone	425	1:1	26	60	72	4.5	5.56
					135	72	4.6	5.23
					240	72	5.0	4.79
60,000	Dolomitic Limestone	439	1:1	22	80	80	2.4	831
					270	78	3.0	330

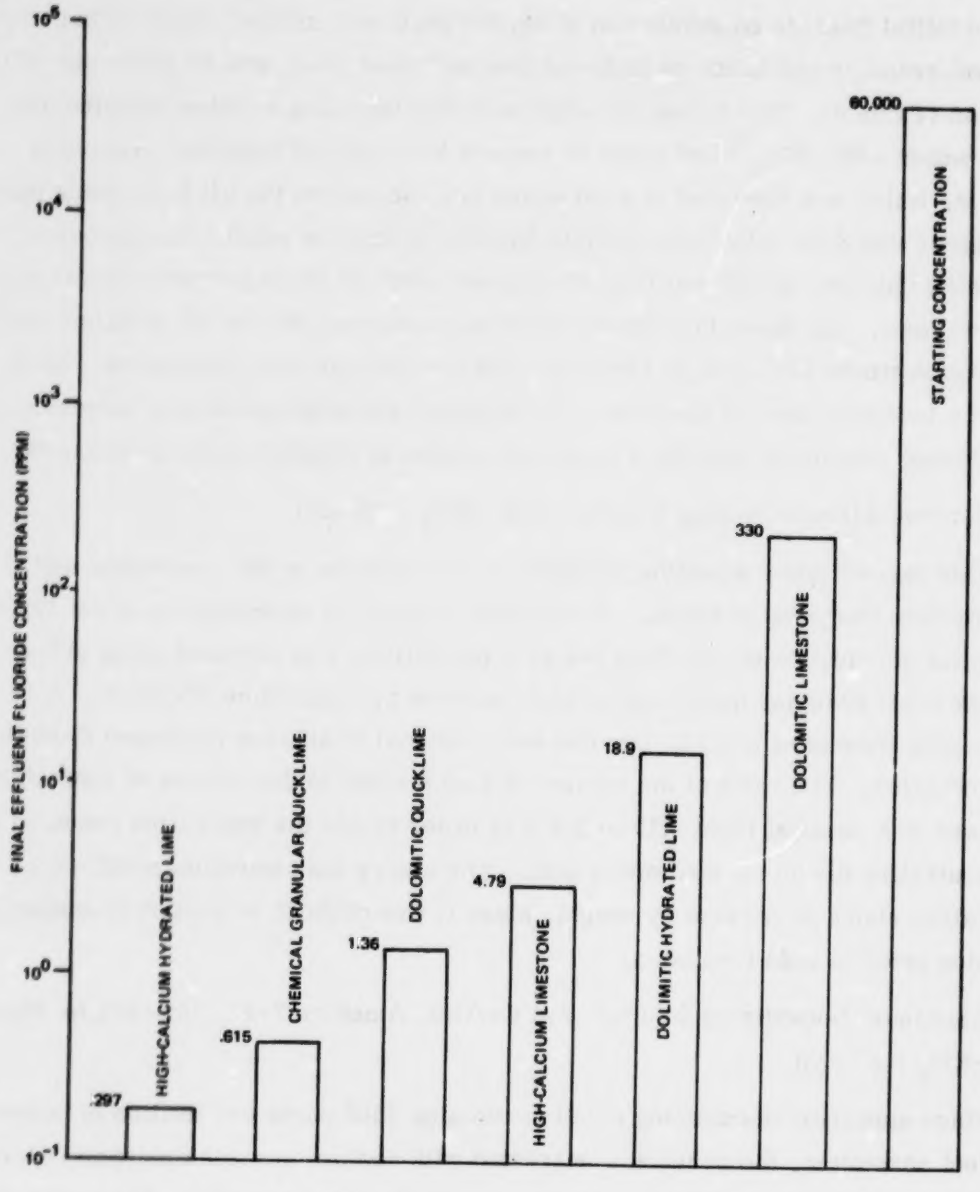

Figure 3. **Lime Treatment of 40% Nitric Acid (42° Bē) by Volume/2% Hydrofluoric Acid (70% Weight) by Volume Titanium Pickling and Descaling Solution**

aluminum deoxidizing and aluminum conversion coating solutions tested with chemical granular quicklime and high-calcium hydrated lime.

Ferrous Alloy Descaling Solution (5% H_2SO_4 - 3 Oz/Gal. $NaNO_3$ - 3 Oz/Gal. Actane 70)

The lowest fluoride level that could be achieved with this solution, which had an initial fluoride concentration of 16,000 parts per million, using either chemical granular quicklime or high-calcium hydrated lime, was 29 parts per million (Table 6). The Actane 70 additive to the descaling solution contains ammonium salts (NH_4^+) and about 76 percent by weight of fluoride. Ammonia gas, which was liberated at a pH above 7.0, prevented the pH from going much higher that 8.0. Since the calcium flouride formed is soluble in ammonium salt solutions, an effluent fluoride content below 29 parts per million was not produced. As shown in Table 6, more ammonia was driven off at higher retention times while the pH increased and the fluoride level decreased. Even at a retention time of five hours for chemical granular quicklime, however, an effluent containing only 29.0 parts per million of fluoride could be obtained.

Ferrous Alloy Descaling Solution (50% HNO_3 - 5% HF)

This ferrous alloy descaling solution is very similar to the previously tested titanium descaling solution. A reduction in fluoride concentration from 39,600 parts per million to less than one part per million was obtained using either chemical granular quicklime or high-calcium hydrated lime (Table 7). A retention time of at least 30 minutes was required to achieve maximum fluoride reduction. The ratio of the volume of acid treated to the volume of lime slurry used was changed from 1:10 to 1:1.6 in order to add the extra lime required to neutralize the 50 percent nitric acid. The slurry concentration could not be raised above 30 percent by weight, since it was difficult to keep it in suspension prior to acid treatment.

Aluminum Deoxidizing Solution (2-6 Oz/Gal. Amchem 7-17, 15%-20% by Volume HNO_3 (42° Bē))

Since aluminum deoxidizing solution contains 5500 parts per million of hexavalent chromium, the solution was treated with sodium metabisulphite to reduce the chromium to the trivalent form prior to fluoride treatment. Treatment with

TABLE 6

LABORATORY LIME TREATMENT RESULTS FOR FERROUS ALLOY DESCALING SOLUTION [SULFURIC ACID (2-10%) + SODIUM NITRATE (1-5 OZ/GAL) + ACTANE 70 (1-5 OZ/GAL)]

Initial Fluoride Concentration (ppm)	Lime Used For Treatment	Slurry Concentration (gram/liter)	Volume Acid: Volume Slurry	Temp. Increase During Neutralization (°F)	Solids Retention Time (minutes)	Effluent Temp. Prior To Solids Separation (°F)	Effluent pH	Effluent Fluoride Concentration (ppm)
16,000	Chemical Granular Quicklime	202	2:1	24	5	128	2.3	2,990
					15	115	2.4	2,580
					30	110	2.9	1,750
					60	96	3.7	540
					150	80	8.4	48
					180	80	8.3	41
					240	78	8.7	40
					300	78	8.7	29
16,000	High-Calcium Hydrated Lime	267	2:1	56	5	-	5.8	64.5
					15	-	7.4	40.0
					30	100	7.7	41.5
					105	82	7.9	46.8
					180	78	8.2	38.9
					240	74	8.2	36.2

TABLE 7

LABORATORY LIME TREATMENT RESULTS FOR FERROUS ALLOY DESCALING SOLUTION (50% NITRIC ACID + 5% HYDROFLUORIC ACID)

Initial Fluoride Concentration (ppm)	Lime Used For Treatment	Slurry Concentration (grams/liter)	Volume Acid: Volume Slurry	Temp. Increase During Neutralization (°F)	Solids Retention Time (minutes)	Effluent Temp. Prior To Solids Separation (°F)	Effluent pH	Effluent Fluoride Concentration (ppm)
39,600	Chemical Granular Quicklime	244	1:1.6	94	15	136	10.6	4.38
					30	116	10.8	0.43
					60	94	11.2	0.93
					120	84	11.2	1.12
39,600	High-Calcium Hydrated Lime	322	1:1.6	88	15	130	10.6	4.65
					30	116	11.2	0.78
					60	98	11.2	1.59
					120	88	11.2	2.87
					240	84	11.3	2.16

20 grams of dry $Na_2S_2O_5$ per liter of waste produced a solution containing less than 0.1 part per million of hexavalent chromium. Chemical granular quicklime gave optimum results on aluminum deoxidizing solution (Table 8). The initial fluoride concentration was reduced from 2250 parts per million to less than one part per million using a 176 gram-per-liter slurry and a waste-to-slurry ratio of 5:4. Although the solids retention time required was three hours, the fluoride concentration could be reduced to less than three parts per million in 15 minutes. The lowest fluoride concentration that could be achieved with high-calcium hydrated lime at a slurry concentration of 232 grams per liter and a waste-to-slurry ratio of 5:4 was 3.45 parts per million. The solids retention time was 30 minutes.

Aluminum Conversion Coating Solution (Alodine 1200)

The aluminum conversion coating solution, which contains 1000 parts per million of hexavalent chromium, was treated with sodium metabisulphite to reduce the chromium to the trivalent form prior to fluoride treatment. Treatment with 4.16 grams per liter of dry sodium metabisulphite reduced the hexavalent chromium concentration to less than 0.1 part per million. The chromate-reduced Alodine 1200 solution was treated with 25.6 grams of dry chemical granular quicklime per liter of waste. Fluoride concentration was reduced from 1750 to 19.4 parts per million with a 25-minute retention time (Table 9). The lowest fluoride level that could be obtained using high-calcium hydrated lime at a concentration of 17 grams (dry) per liter of waste was 23.2 parts per million for a retention time of one hour. Since Alodine 1200 contains ammonium bifluoride, ammonia gas was liberated during lime treatment until equilibrium was established. The solubility of precipitated calcium fluoride in the remaining ammonium salt prevented the fluoride concentration from being reduced below 19.4 parts per million. A secondary treatment will be required on this solution to produce an effluent containing less than three parts per million of fluoride.

SELECTION AND EVALUATION OF ION-EXCHANGE MATERIALS

Manufacturers of ion-exchange materials, sales representatives and literature were consulted to determine those ion-exchange materials which could best be utilized to remove fluorides from acid rinse waters. Based on this search, the following three materials were selected for study:

TABLE 8

LABORATORY LIME TREATMENT RESULTS FOR ALUMINUM DEOXIDIZER SOLUTION (2-6 OZ/GAL. AMCHEM 7-17 DEOXIDIZER + 15-20% NITRIC ACID)

Initial Fluoride Concentration (ppm)	Lime Used For Treatment	Slurry Concentration (gram/liter)	Volume Acid: Volume Slurry	Temp. Increase During Neutralization (°F)	Solids Retention Time (minutes)	Effluent Temp. Prior To Solids Separation (°F)	Effluent pH	Effluent Fluoride Concentration (ppm)
2,250	Chemical Granular Quicklime	176	5:4	30	5	118	11.6	4.94
					15	94	11.6	2.71
					30	84	11.4	2.70
					60	77	11.5	1.53
					180	76	11.5	0.76
					260	76	11.5	1.23
2,250	High-Calcium Hydrated Lime	232	5:4	40	15	108	10.6	5.95
					30	88	10.9	3.45
					60	82	11.0	4.09
					120	76	10.9	3.47
					255	76	10.0	3.07

TABLE 9

LABORATORY LIME TREATMENT RESULTS FOR ALUMINUM CONVERSION COATING (ALODINE 1200)

Initial Fluoride Concentration (ppm)	Lime Used For Treatment	Dry Lime Concentration (grams/liter)	Temp. Increase During Neutralization (°F)	Solids Retention Time (minutes)	Effluent Temp. Prior To Solids Separation (°F)	Effluent pH	Effluent Fluoride Concentration (ppm)
1,750	Chemical Granular Quicklime	25	9	25	80	10.3	19.4
				40	80	10.9	41.6
				55	78	11.1	42.8
				80	78	11.7	43.0
				140	76	12.3	21.4
				240	76	12.2	20.8
				300	76	12.3	17.4
1,750	High-Calcium Hydrated Lime	17	4	5	77	8.3	62.5
				15	77	9.0	38.0
				30	77	8.8	31.4
				60	77	8.7	23.2
				195	77	8.6	47.2
				240	77	8.6	45.4

- Ionac P-60 Resin, Ionac Chemical Corporation
  - Chemical Properties - A proprietary formulation which will remove fluoride ions from water if specific conditions are met.
  - Physical Properties
    - Bulk Density: 50-55 lbs/ft^3
    - Mesh: -16 + 50
    - Moisture content as shipped: About 30%
  - Cost - $20.00 per cubic foot
- Amberlite IRA-400 Resin, Rohm and Haas
  - Chemical Properties - A strongly basic ion-exchange material consisting of an 8% cross-linked polystyrene matrix of the trimethylbenzylammonium type
  - Physical Properties
    - Bulk Density: 44 lb/ft^3
    - Mesh: 20-50
    - Void Volume: 40-45%
    - Moisture Content (Drained): 55% by weight
  - Cost - $61.40 per cubic foot
- F-1 Activated Alumina, Aluminum Corporation of America
  - Chemical Properties - A porous form of aluminum oxide having a high surface area
  - Physical Properties
    - Bulk Density: 55 lb/ft^3
    - Size: 1/4" to 8 mesh
    - Moisture Content (Drained): 44% by weight
  - Cost - $9.30 per cubic foot

These materials were evaluated according to the criteria set forth in the fourth edition of Perry's Chemical Engineering Handbook by obtaining isotherm, breakthrough, regeneration and rinse data.

DEVELOPMENT OF ISOTHERM DATA PROCEDURES

The fluoride rinse solutions under study can be considered as one of the simplest forms of ion-exchange systems - namely a solvent or carrier and the solute. Simple plots could readily be drawn of the solute concentrations in the solid phase as a function of its concentration in the fluid phase. Since this functional relationship holds true at one particular temperature, these plots are known as isotherms.

Separation performance depends upon the curvature of a particular isotherm; usually a convex-upward curve would signify favorable exchange and a concave-upward curve would signify unfavorable conditions. However, these curves should not be used solely as a basis for discarding a resin system; a concave-upward curve does not mean a system won't work, but that more resin than expected will have to be used to achieve the desired results.

The isotherm data was obtained by placing a known weight of resin in a 250-ml plastic jar and then adding a 200-ml aliquot of a known concentration of sodium fluoride solution. The bottle was shaken for two hours on a vibrating table and then left standing for 24 hours. A sample of the liquid phase was drawn off and analyzed for fluoride. Before being used for this test, the resins were regenerated as follows:

- Ionac P-60 Resin
  - Regenerate with 5% sodium hydroxide, using a dosage of 4 lbs/ft^3
  - Rinse with water at a rate of 1 gpm/ft^3 for a total of 15 gallons
  - Neutralize with 1% potassium bisulfate solution, using a dosage of 1 lb/ft^3
  - Rinse with water at a rate of 1 gpm/ft^3 for a total of 30 gallons
- Amberlite IRA-400 Resin
  - Regenerate with 4% sodium hydroxide, using a dosage of 6 lbs/ft^3

  - Rinse with water at a rate of 0.25 gpm/1-bed volume and then at a rate of 1.5 gpm/ft^3 resin until a pH of 10 is reached

- Alcoa F-1 Activated Alumina
  - Regenerate with 4% sulfuric acid using a dosage of 12 lbs/ft^3
  - Rinse with water until a pH of 4.7 is reached

The isotherm data was compared with plots on pages 16-5, 16-8, 16-9, and 16-10 of Perry's Chemical Engineering Handbook. The generalized plots show the concentration in the fluid phase, c, as the abscissa. A plot of "q" versus "c", which is convex-upward, is a favorable isotherm. Facile absorption of material from the fluid phase onto the solid phase will occur. For simplicity, the symbols defined below will be used throughout this report:

c = concentration in stream at equilibrium

C_o = initial concentration in stream (influent)

q = concentration in resin at equilibrium

Q = upper limit of concentration in resin

For this particular program, Q is the capacity of the resin for fluoride. This is the total fluoride which the resin can absorb when fluoride breakthrough is seen in the effluent. Then q/Q is the degree of exhaustion of the resin. When $q/Q = 1$, the resin has absorbed as much of the fluoride as it can (vertical saturation). At this point, c/C_o goes to one, since no more flouride is absorbed. This is fluoride breakthrough and signals that the bed must be regenerated.

For the general ion-exchange of solution ion A with resin ion B, the exchange reaction is:

$$A + RB \rightleftarrows RA + B,$$

assuming A and B are of the same valence (true for system under study). Equilibrium is then given by:

$$K_{AB} = \frac{q_A}{c_A} \times \frac{c_B}{q_B} = \frac{Y_A}{X_A} \times \frac{X_B}{Y_B}$$

where q is the concentration of A or B in the resin

c is the concentration of A or B in the solution

Y is the plot of q/Q

X is the plot of c/C_o

Q is the capacity of the resin for A

C_o is the influent concentration of A

The following results were obtained:

- Ionac P-60 Ion-Exchange Resin - The exchange data for the Ionac P-60 resin was so meager that an isotherm plot was not warranted. By comparing C_o (the total concentration of fluoride ions in solution) with C (the equilibrium fluoride concentration), the low fluoride pickup can be seen (Table 10). Since the fluoride pickup was so low, the large volume of P-60 resin that would be required for fluoride removal from the rinse waters to be tested would make its use impractical. As a result, further evaluation of this resin was discontinued.
- Amberlite IRA-400 Ion-Exchange Resin - Analysis of the data obtained for the Amberlite IRA-400 resin (Table 11) shows that the degree of pickup for this resin is much greater than that for the Ionac P-60 resin. The plot of equilibrium concentration of fluoride ions in solution (C) versus the weight of fluoride ion removed over the total weight of absorber (q) in Figure 4 was compared with that of Type V resin (Figure 16-3, page 16-9, of the fourth edition of Perry's Chemical Engineer's Handbook). If the equation is considered to be a Langmuir type, then according to Table 16-5 this resin has unfavorable characteristics at low concentrations and favorable at high concentrations.

TABLE 10

ISOTHERM DATA FOR IONAC P-60 ION-EXCHANGE RESIN AT 26°C

Sample No.	Sample Size (ml)	C_o (mg/l)	W (mg)	w (mg)	$q = \frac{w}{W}$	C (mg/l)	Q	$X = \frac{c}{C_o}$	$Y = \frac{q}{Q}$
1	200	85	5072	1.4	2.76×10^{-4}	78	9.5×10^{-4}	0.917	0.291
2	200	85	4092	0.2	4.9×10^{-5}	84	9.5×10^{-4}	0.987	0.052
3	200	85	2923	0.6	2.06×10^{-4}	82	9.5×10^{-4}	0.964	0.217
4	200	85	1978	1.2	6.19×10^{-5}	79	9.5×10^{-4}	0.929	0.065
5	200	85	946	0.9	9.5×10^{-4}	81	9.5×10^{-4}	0.946	1.000
6	200	85	634	0.4	6.32×10^{-4}	83	9.5×10^{-4}	0.975	0.665

C_o = Total Concentration of F^- ions removed

W = Total weight of adsorber

w = Weight of F^- ions removed

C = Equilibrium F^- ions removed

Q = Capacity of adsorber experimentally determined; for above, $Q = 9.5 \times 10^{-4}$

TABLE 11

ISOTHERM DATA FOR AMBERLITE IRA-400 ION-EXCHANGE RESIN AT 26°C

Sample No.	Sample Size (ml)	C_o (mg/l)	W (mg)	w (mg)	$q = \frac{w}{W}$	C (mg/l)	Q	$X = \frac{C}{C_o}$	$Y = \frac{q}{Q}$
1	200	119	2676	10.9	.00417	64.3	.0658	.540	.0636
2	200	119	2217	11.2	.00507	63.0	.0658	.529	.0775
3	200	119	1787	9.2	.00513	73.0	.0658	.613	.0780
4	200	119	1443	7.4	.00512	82.0	.0658	.689	.0780
5	150	119	582	4.7	.00808	87.7	.0658	.737	.1230
6	200	135	427	6.4	.01500	103.0	.0658	.762	.2290
7	200	135	221	6.0	.02720	105.0	.0658	.777	.4140
8	200	135	127	6.4	.05030	103.0	.0658	.762	.7680
9	200	135	76	5.0	.06580	110.0	.0658	.812	1.0000
10	175	135	45	1.6	.04500	126.0	.0658	.932	.6850
11	200	126	3471	10.4	.00300	74.0	.0658	.588	.0458
12	200	126	6182	15.4	.00249	48.8	.0658	.388	.0380
13	200	119	8924	13.3	.00148	52.4	.0658	.430	.0218
14	200	119	16237	20.6	.00176	15.8	.0658	.131	.0268
15	200	119	16727	20.1	.00121	18.4	.0658	.154	.0184

C_o = Total concentration of F^- ions in solution
W = Total weight of adsorber
w = Weight of F^- ions removed
C = Equilibrium F^- ions removed
Q = Capacity of adsorber experimentally determined; for above, Q = .0658

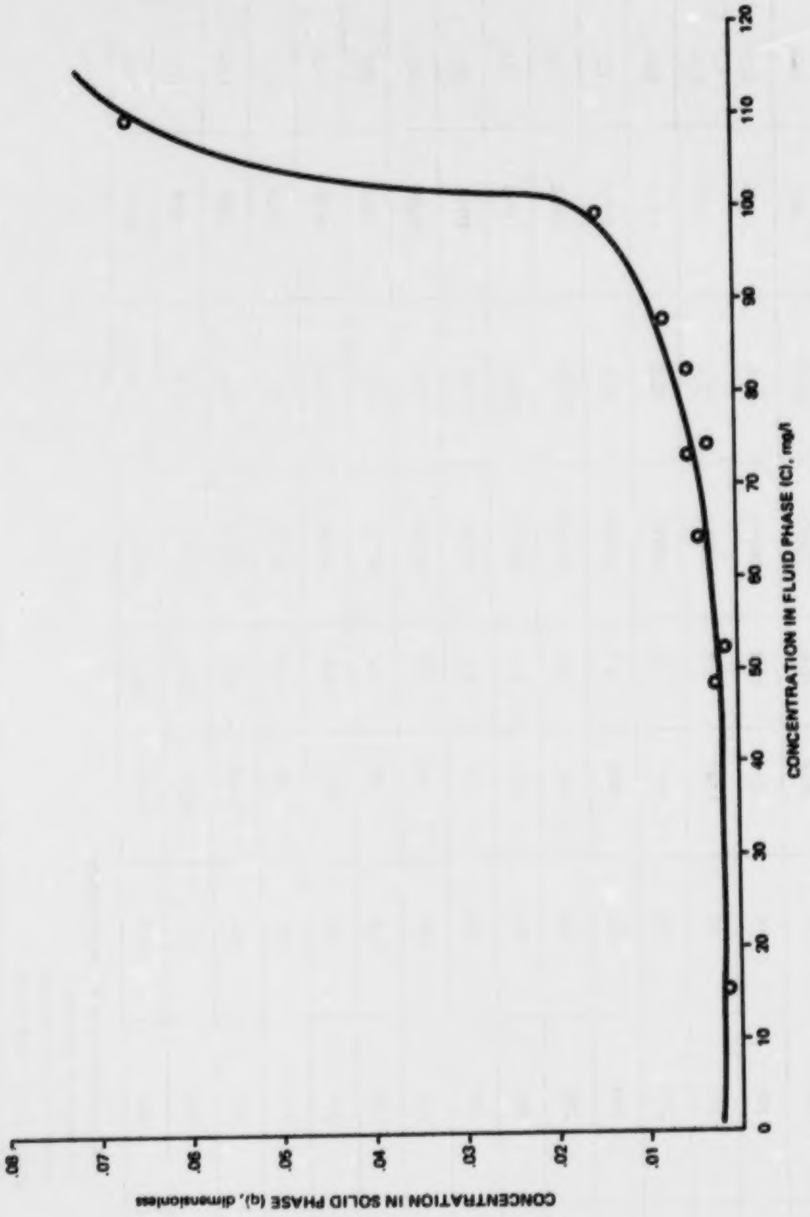

Figure 4. Isotherm Plot for Amberlite IRA-400 Ion-Exchange Resin

- F-1 Activated Alumina Ion-Exchange Material - The isotherm data obtained for the activated alumina (Table 12) was plotted as C versus q (Figure 5) and compared to applicable plots in Perry's Chemical Engineer's Handbook. The curve for the activated alumina was similar to that for the IRA-400 resin. It will be shown subsequently in this section that the exchange characteristics of activated alumina are extremely dependent upon the rate of flow of the solution. The pH regulating capability of the material, however, is excellent and will be used for this purpose and as a fluoride polishing treatment in subsequent evaluations.

GENERATION OF BREAKTHROUGH DATA

In simple fixed-bed operations, the ion being exchanged is removed continously from the carrier fluid and accumulated in the solid phase. Such transfer proceeds until the concentration on the solid reaches a value corresponding to equilibrium with the concentration in the feed stream. Although at this point the fluid just leaving the solid layer at the top of the column reaches the feed concentration, the column effluent remains practically free of this solute until the last layer of the sorbent is nearly saturated. This change in effluent concentration with time is known as breakthrough or concentration history.

Amberlite IRA-400 Resin

Prior to the establishment of breakthrough data for the Amberlite IRA-400/120-135 ppm sodium fluoride solution, the Amberlite resin was activated by flowing 4500 grams of 4% by weight NaOH through it. The resin was rinsed and the pH of the effluent measured (10.5-11.5). The sodium fluoride solution was then passed through the column at a rate of 6.7 gallons per hour. Breakthrough occurred after about 215 liters of 120-ppm fluoride solution were passed through the 3-5/16-inch diameter x 13-inch high Plexiglas column filled with 0.0648 cubic feet of resin.

The breakthrough data was obtained as follows: After a known volume of solution was passed through the column (see Table 13), a 200-ml sample was taken

TABLE 12

ISOTHERM DATA FOR ALCOA F-1 ACTIVATED ALUMINA ION-EXCHANGE MATERIAL AT 26°C

Sample No.	Sample Size (ml)	C_o (mg/l)	W (mg)	w (mg)	$q = \frac{w}{W}$	C (mg/l)	Q	$X = \frac{C}{C_o}$	$Y = \frac{q}{Q}$
1	200	135	1200	5.0	.00416	110.0	.0326	.8150	.128
2	200	135	1004	9.6	.00958	87.1	.0326	.6450	.294
3	200	135	801	7.7	.00950	96.5	.0326	.7150	.291
4	200	135	601	5.6	.00932	107.0	.0326	.7900	.286
5	200	135	306	2.6	.00852	122.0	.0326	.9020	.261
6	200	135	214	2.8	.01310	121.0	.0326	.8970	.402
7	200	135	130	2.2	.01690	124.0	.0326	.9200	.518
8	200	135	67.2	1.0	.01490	130.0	.0326	.9630	.458
9	200	135	43.0	1.4	.03260	128.0	.0326	.9500	1.00
10	200	135	20.9	0.6	.02940	132.0	.0326	.9780	.900
11	200	135	14999	24.0	.00160	14.8	.0326	.1096	.049
12	200	135	8376	25.0	.00298	10.2	.0326	.0756	.092

C_o = Total concentration of F^- ions in solution
W = Total weight of adsorber
w = Weight of F^- ions removed
C = Equilibrium F^- ion concentration
Q = Capacity of adsorber experimentally determined; for above, Q = .0326

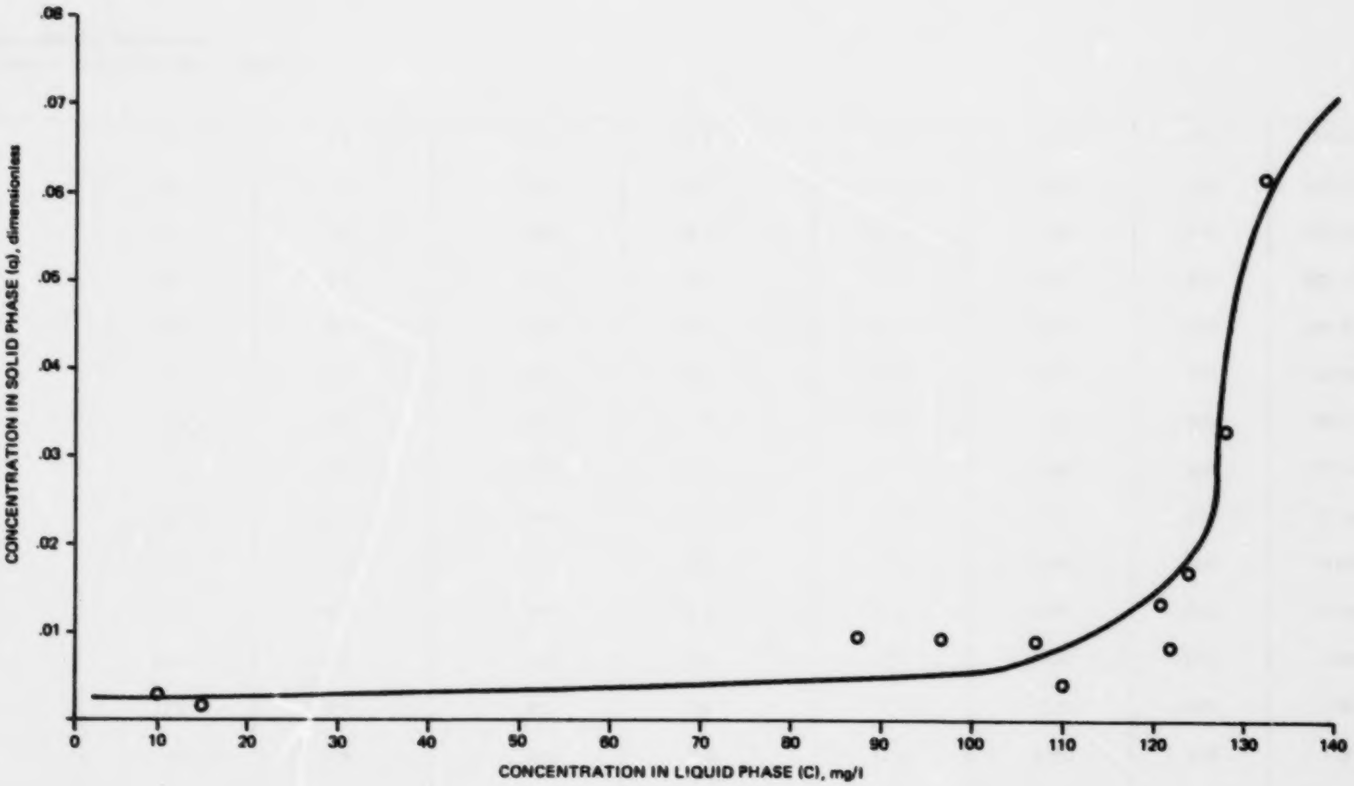

Figure 5. Isotherm Plot for Alcoa F-1 Activated Alumina Ion-Exchange Material

TABLE 13. COLUMN BREAKTHROUGH DATA FOR AMBERLITE IRA-400 ION-EXCHANGE RESIN AND SODIUM FLOURIDE SOLUTION (119-124 PARTS PER MILLION OF FLUORIDE ION) AT 26°C

Sample No.	Fluoride Input (ppm)	Input pH	Input Cond. (µmhos/cm)	Fluoride Output (ppm)	Exit pH	Exit Cond. (µmhos/cm)	Sample Size (ml)	Volume Passed (ml)
1	119	6.4	545	0.3	11.0	380	200	400
2	119	6.4	545	0.3	11.6	1180	200	1,000
3	119	6.4	545	0.6	11.5	1200	200	2,000
4	119	6.2	545	0.8	11.6	1150	200	3,600
5	119	6.2	545	0.2	11.6	1100	200	4,800
6	119	6.2	545	0.8	11.6	1000	100	6,500
7	118	6.3	515	0.6	11.6	1120	200	13,700
8	117	6.6	535	0.9	11.6	1160	200	25,900
9	126	6.6	530	1.8	11.8	1140	200	39,920
10	124	6.9	500	4.0	11.6	1240	200	98,250
11	124	6.9	500	16.0	11.7	1280	200	163,885
12	124	6.9	500	9.9	11.7	1250	200	168,085
13	124	6.9	500	18.3	11.7	1260	200	181,035
14	124	6.9	500	89.5	11.4	1230	200	219,920
15	124	6.9	500	119.0	11.0	1200	200	229,255

Column = 3 5/16 DX13H = .065 ft^3
Flow Rate 6.7 Gallons/Hour

and analyzed. This procedure was repeated until about 230 liters had been processed. A plot of the data (Figure 6) showed that breakthrough (inflection point) occurred at about 215 liters.

Alcoa F-1 Activated Alumina

Activated alumina (0.07 cubic feet) was placed in the 3-5/16-inch-diameter x 13-inch-high Plexiglas column. The alumina was activated by passing 8850 grams of 4% by weight H_2SO_4 through it. The activated alumina was rinsed with one liter of water at a rate of 7.10 gallons per hour and then rinsed with 15 liters of water at a rate of 24.2 gallons per hour. The pH of the water at this point was 3.6. A standard sodium fluoride solution containing 130 parts per million of fluoride ion was passed through the column. After 13.6 liters had been passed through the column, it was observed that the effluent fluoride concentration was very erratic. Two batches of solution were then passed backward through the column to determine if better solution/alumina contact would improve results. The same erratic results were again obtained. The sodium fluoride was then continued through the column in a forward direction until 52.4 liters had been passed. It was concluded that significant breakthrough data could not be obtained, since the exchange operation was extremely flow rate-dependent (see Table 14). It was observed, however, that the input pH and the exit pH were very close in value. Since the ultimate objective of this experiment was to keep a captive rinse (that is, to take process water, remove the fluoride and then replace the water in the rinse tank), the pH of the water going back into the tank would have to approximate the pH of the rinse before exchange. Therefore, 10 liters of the effluent obtained from the IRA-400 study were passed through the alumina F-1 column. The influent had a pH of about 11 and the effluent had a pH of about 5.5. The F-1 activated alumina, in addition to its ion-exchange properties, did serve as a pH regulating agent. It was decided to use a two-stage, ion-exchange system for the chemical milling rinse studies. The first column would contain Amberlite IRA-400 resin to remove the bulk of the fluoride; the second column would contain Alcoa F-1 activated alumina mainly for pH control and for some limited ion-exchange.

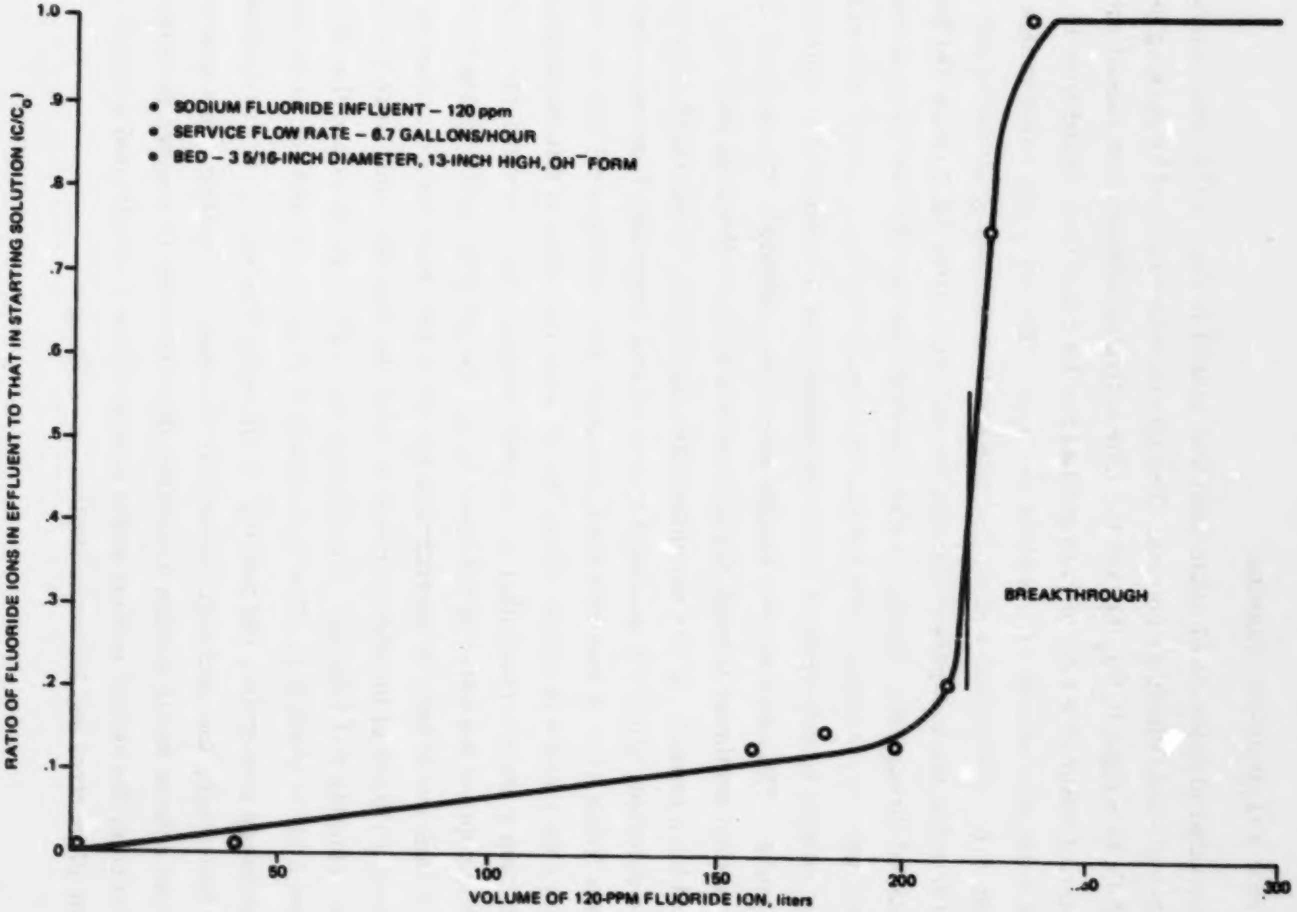

Figure 6. Amberlite IRA-400 Ion-Exchange Resin Breakthrough Curve

TABLE 14. COLUMN BREAKTHROUGH DATA FOR ALCOA F-1 ACTIVATED ALUMINA AND SODIUM FLUORIDE SOLUTION (130 PARTS PER MILLION OF FLUORIDE ION)

Flow Mode	Fluoride Input (ppm)	Input pH	Fluoride Exit (ppm)	Exit pH	Sample Size (ml)	Total Volume Passed (ml)	Flow Rate (gph)
Forward	130	6.5	115.0	6.8	200	4,200	27.20
Forward	130	6.5	9.3	6.2	200	8,400	7.88
Forward	130	6.5	77.4	6.7	200	13,600	5.20
Forward	130	6.5	108.0	7.0	200	18,800	27.20
Backward	130	6.5	80.6	5.7	200	24,000	27.20
Backward	130	6.5	102.0	4.3	200	28,200	27.20
Forward	130	6.5	99.0	4.9	200	32,400	27.20
Forward	130	6.5	15.3	5.2	200	46,000	2.78
Forward	130	6.5	16.2	5.5	200	48,200	2.78
Forward	130	6.5	48.0	6.2	200	52,400	2.78

Column - 3 5/16 inches in diameter by 13 inches high

REGENERATION OF SPENT AMBERLITE IRA-400 RESIN

After passing 230 liters of 120 parts per million fluoride solution through the Amberlite resin, the column had to be regenerated (breakthrough point passed). Again, 4.5 liters of 4% by weight NaOH were passed at a rate of 2.5 gallons per hour in a forward-flow direction. At various volume increments, samples were drawn and the fluoride concentration and pH of the effluent were measured (see Table 15 and Figure 7).

The bed was then rinsed with distilled water (2.5 gallons per hour for one bed-volume and 3.65 gallons per hour for 6.2 bed-volumes). Fluoride concentration and pH of the effluent were measured (see Table 16 and Figure 8). At the end of 7.2 bed volumes of rinse, the pH of the effluent was 10.6 and the fluoride concentration was less than 0.02 part per million.

DEVELOPMENT OF TWO STAGE, ION-EXCHANGE SYSTEMS FOR TITANIUM CHEMICAL MILLING RINSE WATER

A two-stage, ion-exchange system was designed and fabricated (Figure 9) to establish fluoride removal capability on actual titanium chemical milling rinse water. The columns for holding Amberlite IRA-400 ion-exchange resin and Alcoa F-1 activated alumina were constructed of two-inch-diameter by 36-inch-high acrylic tubing. Polyvinyl chloride valves and piping were used. The Amberlite IRA-400 resin used was the regenerated material from the 120-ppm sodium fluoride breakthrough test. The Alcoa F-1 activated alumina was virgin material regenerated with sulfuric acid as previously described. The chemical milling rinse water tested had a fluoride concentration range of 3 to 61 parts per million (average value of 15.8 parts per million). The rinse water also contained nitrate up to 200 parts per million and trace quantities of aluminum, copper, vanadium, tin and iron. The rinse water was flowed through the series of columns at rates ranging from 2.4 to 20.2 gallons per hour. Samples of the effluent effluent were taken at various intervals as described previously. A total 421.7 liters of rinse water was passed through the columns. Breakthrough occurred after 375 liters (100 gallons) of rinse water were passed through (see Table 17 and Figure 10). The results of this test showed that the use of Amberlite IRA-400 resin, in conjunction with Alcoa F-1 activated alumina, is an efficient means of removing fluoride from chemical milling rinse water while simultaneously maintaining the pH of the solution.

TABLE 15. REGENERATION OF AMBERLITE IRA-400 ION-EXCHANGE RESIN WITH 4% BY WEIGHT SODIUM HYDROXIDE

Sample	Flow Mode	Exit Fluoride (ppm)	Exit pH	Sample Volume (ml)	Volume Passed (ml)	Flow Rate (gph)
1	Forward	5520	12.60	4000	4000	2.5
2	Forward	850	12.90	200	4200	2.5
3	Forward	306	13.65	200	4400	2.5
4	Forward	280	13.60	100	4500	2.5

Column - 3 5/16 inches in diameter by 13 inches high

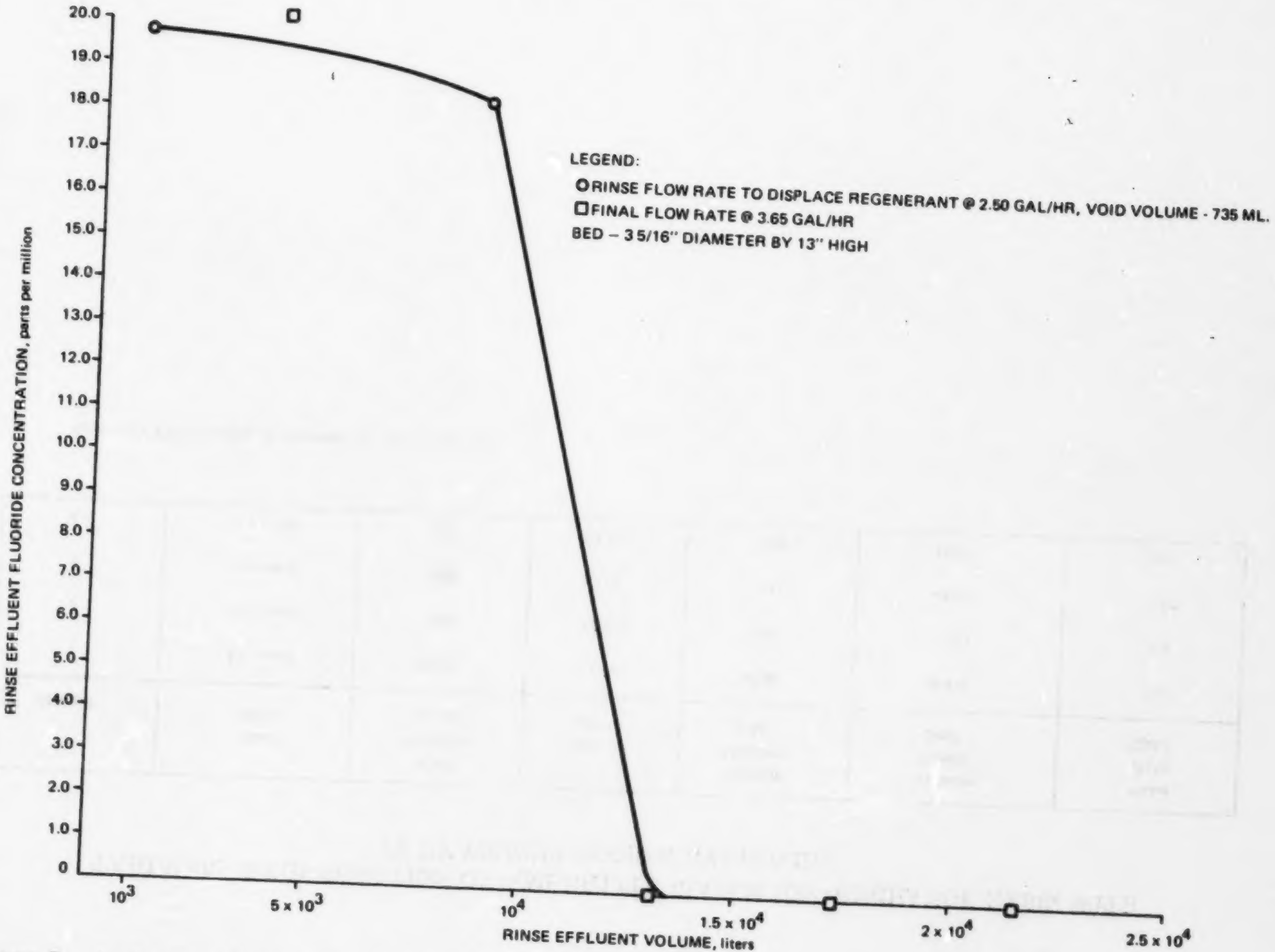

Figure 7. Amberlite IRA-400 Ion-Exchange Resin Rinse Curve for First-Run Spent Tower Following Regeneration

TABLE 16. RINSE WATER PROPERTIES FOLLOWING REGENERATION OF AMBERLITE IRA–400 RESIN BY 4% SODIUM HYDROXIDE

Sample	Flow Mode	Input pH	Exit pH	Exit Fluoride Concentration (ppm)	Sample Volume (ml)	Total Volume Passed (ml)	Flow Rate (gph)
1	Forward	5.65	12.8	19.7	200	1,000	2.50
2	Forward	5.65	12.7	21.5	200	4,200	3.65 (After total of 1.84 liters (passed)
3	Forward	5.65	12.3	18.2	200	8,900	3.65
4	Forward	5.65	10.6	< 0.02	200	13,100*	3.65
5	Forward	5.65	10.6	< 0.02	200	17,300	3.65
6	Forward	5.65	10.2	< 0.02	200	21,500	3.65

Notes: (1) Input Sodium Fluoride Concentration - 120 parts per million
(2) Column Dimension - 3 5/16 inches diameter by 13 inches high

* 7.2 Bed volumes

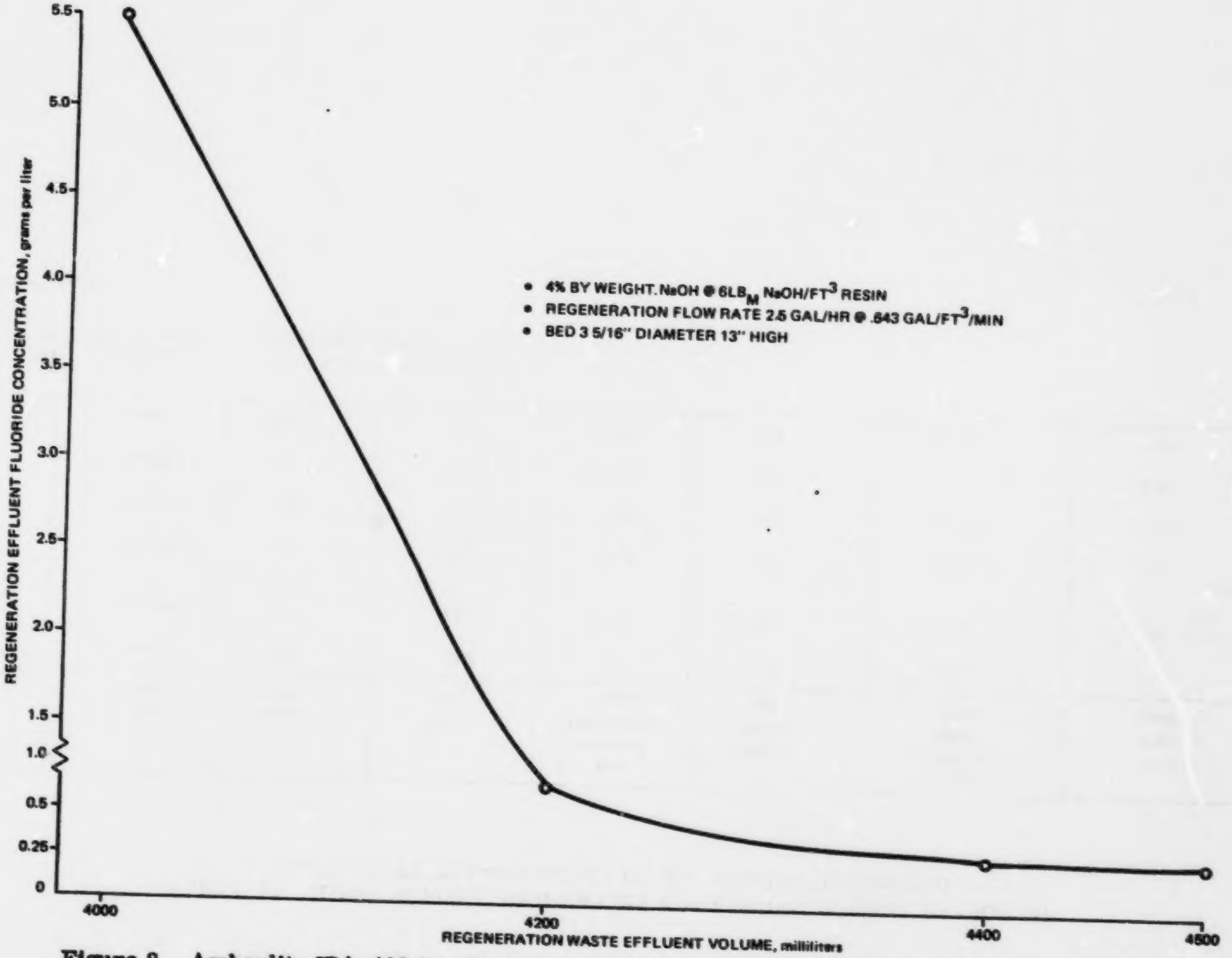

Figure 8. Amberlite IRA-400 Ion-Exchange Resin Regeneration Curve for First-Run Spent Tower

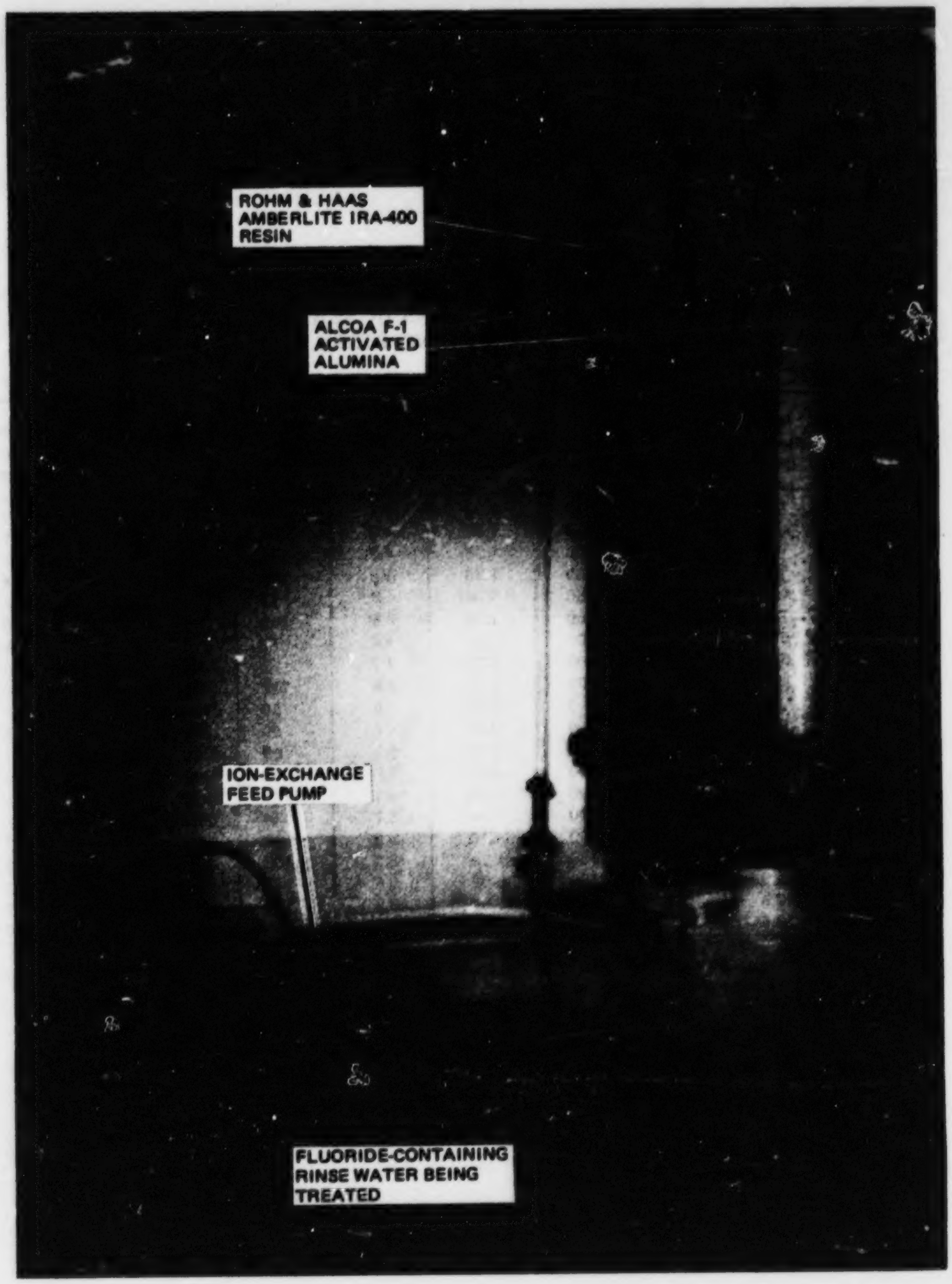
ROHM & HAAS
AMBERLITE IRA-400
RESIN
ALCOA F-1
ACTIVATED
ALUMINA
ION-EXCHANGE
FEED PUMP
FLUORIDE-CONTAINING
RINSE WATER BEING
TREATED

Figure 9. Two-Stage, Ion-Exchange System for Titanium Chemical Milling Rinse Water

TABLE 17
BREAKTHROUGH DATA FOR AMBERLITE IRA-400 RESIN AND ALCOA F-1 ACTIVATED ALUMINA COLUMNS IN SERIES FOR TITANIUM CHEMICAL MILLING RINSE WATER

Sample	Input Fluoride (ppm)	Input pH	Input Cond. (µmhos/cm)	Exit Flouride (ppm)	Exit pH	Exit Cond. (µmhos/cm)	Sample Size (ml)	Total Volume Passed (ml)	Flow Rate (gph)
1	12.1	2.9	1330	1.33	3.1	570	200	10,200	7.0
2	8.85	3.3	360	1.68	4.3	180	200	23,400	4.1
3	8.85	3.3	360	1.38	4.3	140	200	43,400	8.2
4	8.85	3.3	360	1.83	4.3	180	200	49,800	9.3
5	12.1	2.8	1150	0.70	4.8	112	200	124,030	4.2
6	12.1	2.8	1150	1.04	4.5	280	200	132,930	13.6
7	61.1	2.6	1700	1.02	4.4	77	200	153,850	2.4
8	61.1	2.6	1700	1.63	4.7	62	200	173,230	18.3
9	3.08	2.9	790	1.12	4.8	112	200	201,430	16.0
10	3.08	2.9	790	1.02	4.8	50	200	212,130	17.7
11	17.8	2.7	1500	0.44	4.6	69	200	224,330	18.6
12	17.8	2.7	1500	0.15	4.9	58	200	236,530	18.1
13	17.8	2.7	1500	0.82	5.0	57	200	248,730	18.0
14	10.6	2.8	1900	0.60	5.1	55	200	260,930	18.5
15	10.6	2.8	1900	0.94	5.7	74	200	273,130	16.7
16	10.6	2.8	1900	1.10	5.3	57	200	290,580	20.2
17	12.3	2.7	1100	1.70	6.2	108	200	373,130	17.2
18	12.9	2.9	1100	8.00	5.8	117	200	385,130	17.2
19	12.9	2.9	660	10.60	3.9	195	200	409,530	17.2
20	12.6	3.3	660	11.70	4.7	180	200	421,780	17.2

Column Dimensions: Amberlite IRA-400 (2 inch diameter by 32 inches high) and Alcoa F-1 Activated Alumina (2 inch diameter by 31 inches high).

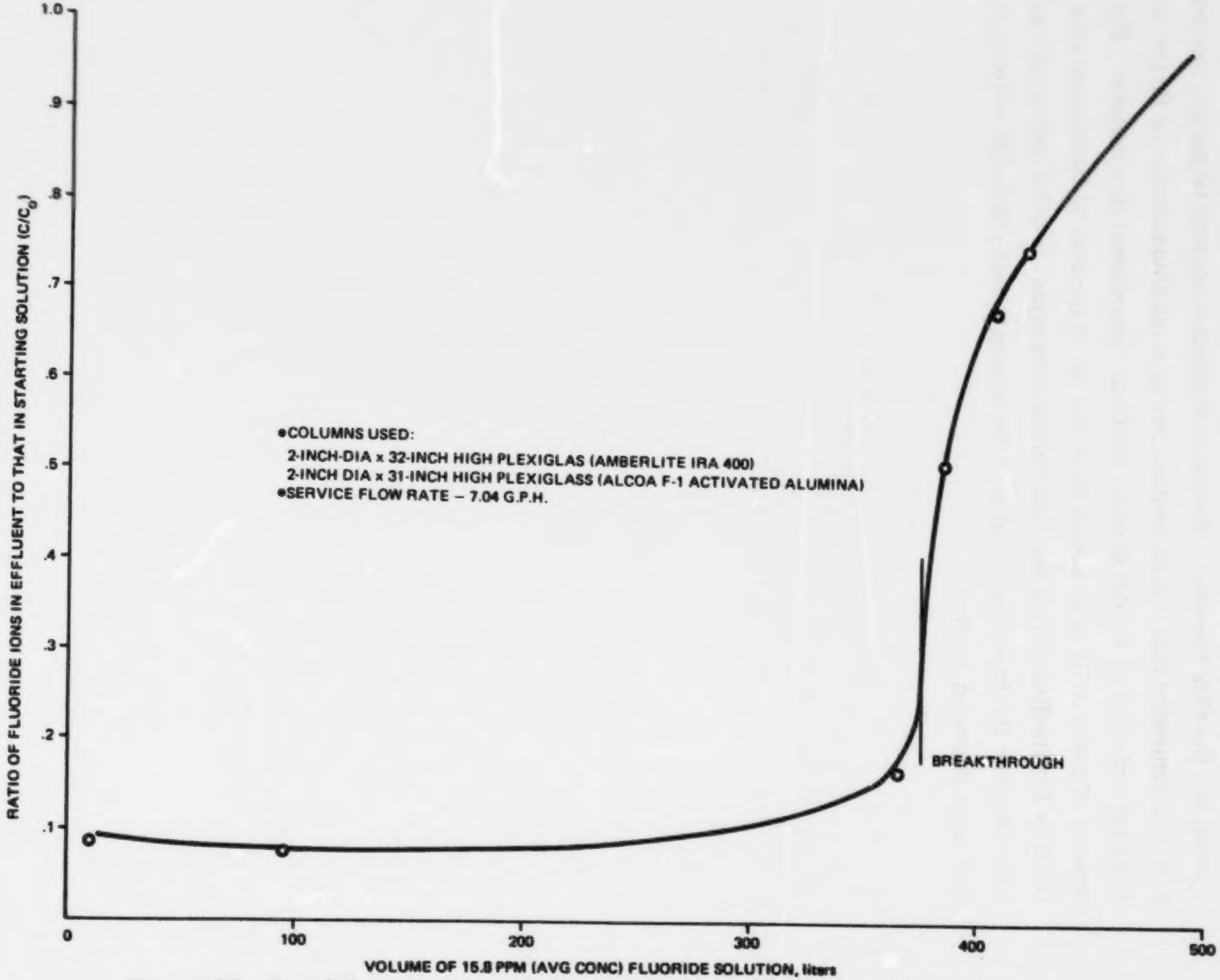

Figure 10. Breakthrough Curve for Titanium Chemical Milling Rinse Water

The laboratory test showed the feasibility of using the series ion-exchange system for fluoride removal. Before a production system is set up, however, it is recommended that a pilot system having a minimum scale-up factor of eight be evaluated to establish more realistic operational parameters. The amount of resin to be used should be based on 80 percent of laboratory data to allow for inefficiency of the distribution networks. A pilot test would establish whether the functional groups of the strongly basic IRA-400 resin hydrolyze upon repeated cycling.

SECTION V

PILOT CENTRIFUGE TREATMENT - TESTING AND ANALYSIS

APPROACH

This phase of the program was concerned with the development of centrifugal techniques for concentrating and removing precipitated fluorides. Chemical granular quicklime, which provided optimum fluoride removal in the Phase I beaker tests, was used for all pilot tests. Pilot tests were conducted on titanium chemical milling, titanium descaling, Amchem 7-17 deoxidizer and Alodine aluminum coating solutions. The ferrous alloy descaling solution was not evaluated on a pilot basis because of its similarity to the titanium descaling solution.

STUDY AREAS

The task of developing pilot centrifuge treatment and removal techniques for fluoride-containing process solutions consisted of the following technical efforts:

- Pilot centrifuge setup and calibration
- Treatment and centrifugal separation of chemical process solutions

PILOT CENTRIFUGE SETUP AND CALIBRATION

A Sharples/Fletcher Mark III centrifuge (Figure 11) manufactured by the Pennwalt Corporation was used for all laboratory pilot testing. This centrifuge, which has a 14-inch-diameter by 6-inch-high basket and a speed capability of 3250 revolutions per minute, is designed for separation studies and performance analyses to generate data for projected production equipment. The pilot centrifuge system (Figure 12) consists of the following components:

- 55-gallon tank with Lightnin AG-100 air-powered mixer for making up lime slurry
- Vanton PY-60 centrifugal pump to transfer lime to treatment tank
- Treatment tank with Holloway Super electric mixer and Jabsco P-6 centrifugal feed pump
- 30-gallon polyvinyl chloride rectangular tank to receive treated effluent (at rear of centrifuge)

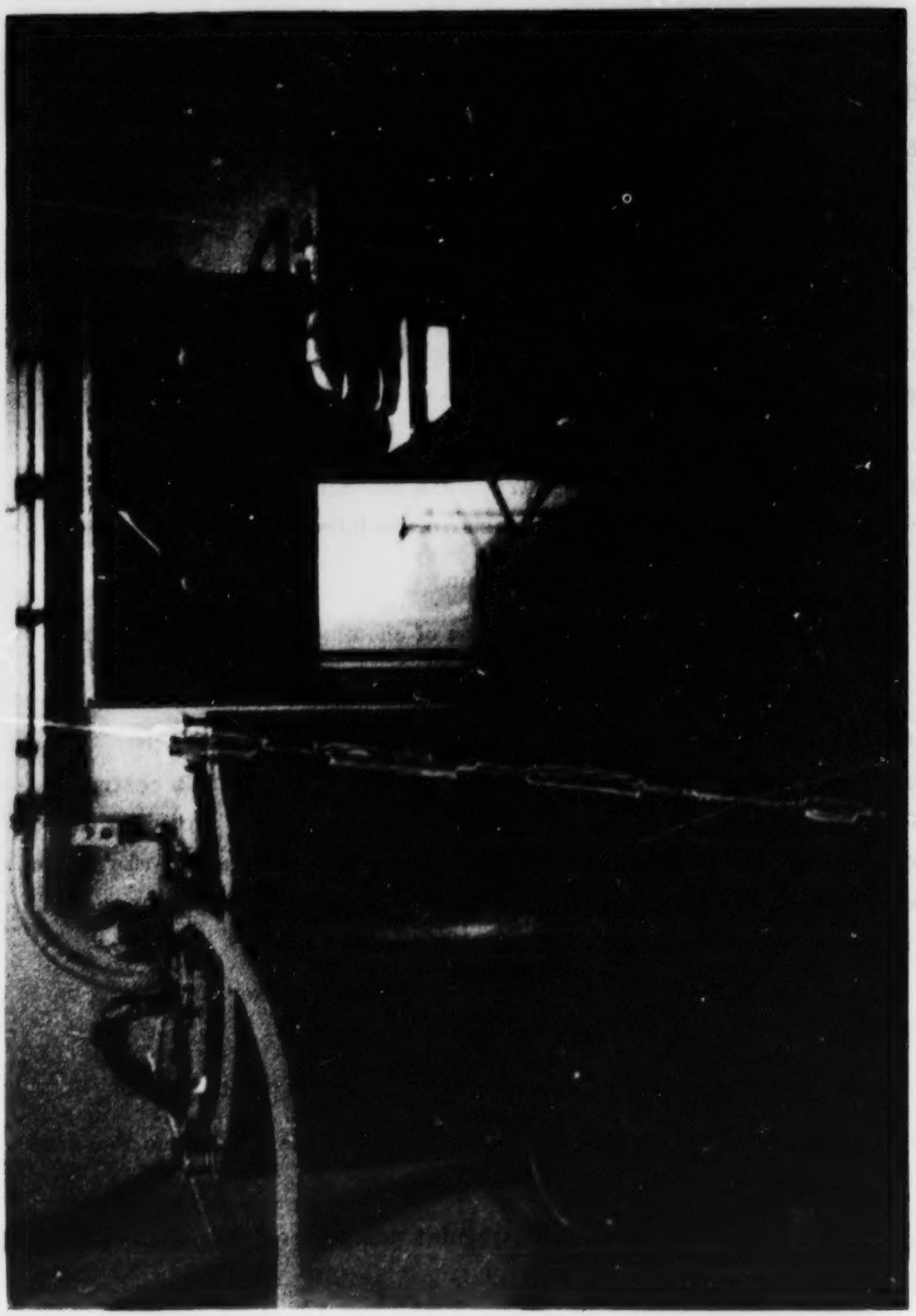

Figure 11. Sharples/Fletcher Mark III Centrifuge

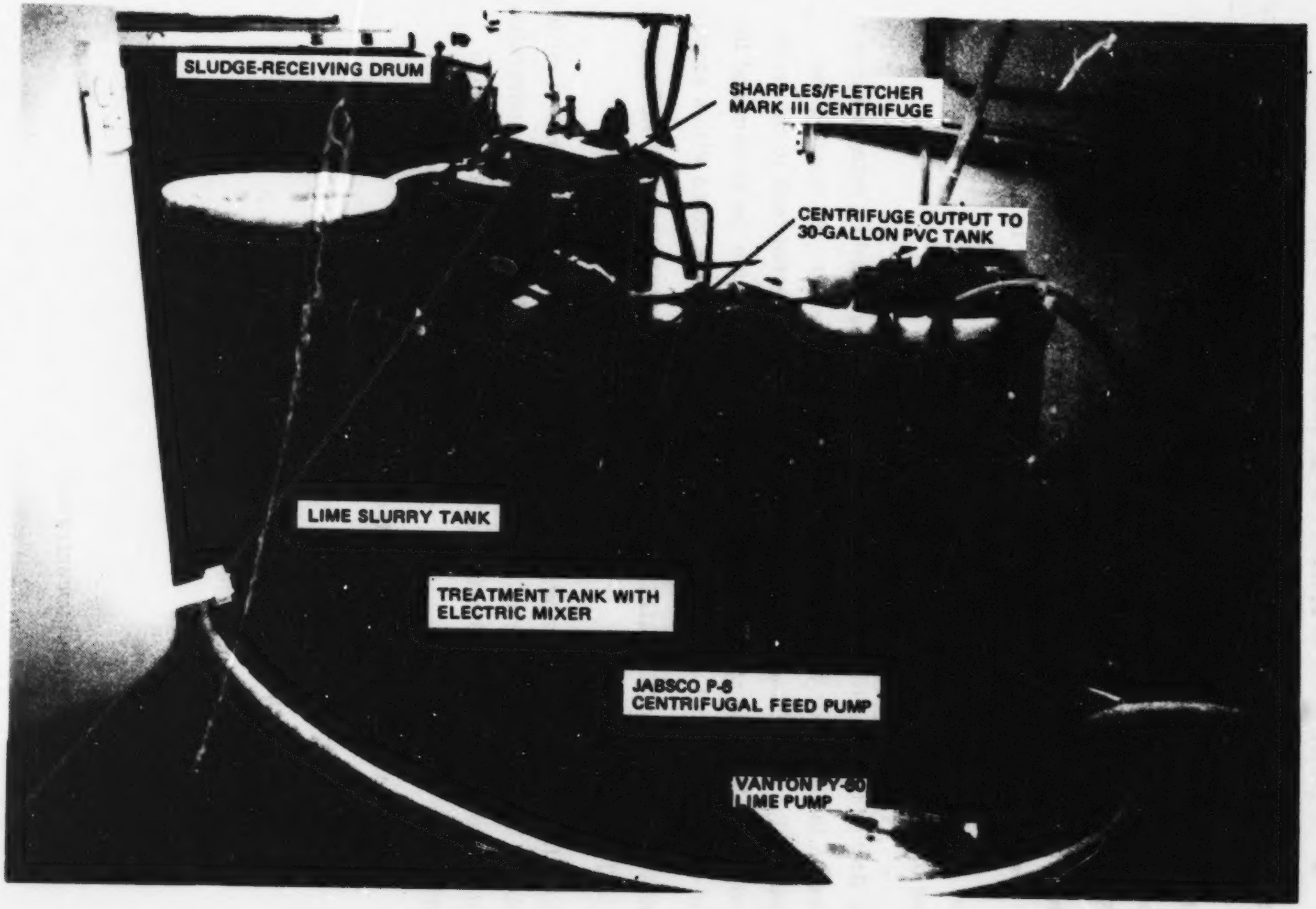
SLUDGE-RECEIVING DRUM
SHARPLES/FLETCHER MARK III CENTRIFUGE
CENTRIFUGE OUTPUT TO 30-GALLON PVC TANK
LIME SLURRY TANK
TREATMENT TANK WITH ELECTRIC MIXER
JABSCO P-6 CENTRIFUGAL FEED PUMP
VANTON PY-50 LIME PUMP

Figure 12. Pilot Centrifuge System

- 55-gallon drum to receive sludge skimmed from centrifuge bowl

The Sharples/Fletcher Mark III centrifuge is completely variable in speed over the 0-3250 rpm range. The Sharples division of the Pennwalt Corporation recommended that testing be conducted at a force of 1300G and flow rates of up to one gallon per minute. The centrifuge speed necessary to obtain the 1300G force was calculated as follows:

Centrifugal force in multiples of the force of gravity

$$= (1.42 \times 10^{-5}) \text{ (Bowl speed in rpm)}^2 \text{ (Bowl diameter in inches)}$$

Bowl speed = 2550 rpm
Bowl diameter = 14 inches

The flow of treated solution to the centrifuge was regulated by using a bypass valve on the exit side of the Jabsco P-6 centrifugal pump. By opening the bypass valve, a portion of the treated solution was diverted back to the treatment tank. Prior to an actual test, water was run through the system and the time necessary to collect a measured amount of water was taken with a stopwatch.

TREATMENT AND CENTRIFUGAL SEPARATION OF CHEMICAL PROCESS SOLUTIONS

Pilot-size treatment parameters were established for titanium chemical milling, titanium descaling, Amchem 7-17 deoxidizer and alodine aluminum conversion coating solutions. The following parameters for pilot-size treatment were established:

- Initial fluoride concentration
- Solution-to-slurry ratio
- Solids retention time
- Temperature increase during treatment
- Flow rate
- Effluent pH
- Effluent fluoride concentration

- Percent solids in effluent
- Density of sludge
- Percent solids in sludge
- Chemical analysis of sludge

Chemical granular quicklime at a slurry concentration of 2.03 pounds of lime per gallon of water was used for all pilot testing. The lime was slaked for 25 to 30 minutes; solution temperature rose 120°F above ambient temperature.

Titanium Chemical Milling Solution

Three pilot tests were conducted on spent titanium chemical milling solution having a fluoride concentration of 93,000 parts per million and an acid concentration of 2.73 normal. Each test was conducted on 10 gallons of spent acid treated with 7.5 gallons of slaked chemical granular quicklime. Specific procedures and results for the three tests conducted were as follows:

- Test No. 1. Ten gallons of titanium chemical milling solution were treated with 7.5 gallons of slaked chemical granular quicklime and mixed with the Holloway Super mixer for one hour. Five gallons of the treated solution were passed through the pilot centrifuge at a rate of 0.6 gallon per minute. Mixing was continued for 6.5 hours, after which an additional five gallons of treated solution were passed through the centrifuge at a rate of 0.6 gallon per minute. The remaining solution was passed through the centrifuge at a rate of 0.6 gallon per minute after 24 hours of mixing. Samples of the centrifuge effluent taken at 1, 6.5-and 24-hour retention times were analyzed and found to contain 8.75, 6.04 and 5.35 parts per million of fluoride, respectively. The calcium flouride sludge was skimmed out of the centrifuge bowl after each test run and physical characteristics were determined. The results of this test are shown in Table 18.
- Test No. 2. This test was conducted in exactly the same manner as test No. 1 except for the mixing technique during solids retention. After treatment with lime, the solution was allowed to stand for 1/2 hour. It was then mixed for one hour. Five gallons of the solution were then

TABLE 18. PILOT CENTRIFUGE TEST RESULTS

FOR CHEMICAL PROCESS SOLUTIONS

Solution	Initial Concentration of Pollutants (ppm)	Ratio of Volume Waste to Volume Slurry	Temperature Rise During Treatment (°F)	Solids Retention Time (hours)	Temperature Of Feed To Centrifuge (°F)	Centrifuge "G" Force	Feed Flow Rate (gpm)	Volume of Solids in Feed, %	pH of Effluent	Volume of Solids in Effluent, %	Bulk Density of Sludge (lbs/ft^3)	Solids In Sludge, %	Volume Of Sludge For 10 Gal. of Feed (gal.)	Sieve Size (mesh)	Effluent Fluoride Concentration (ppm)	Chemical Analysis Sludge (%)
Titanium Chemical Milling (Test No.1)	93,000 Fluoride 2.73 N Acid	4:3	80	1 6.5 24	114 - -	1300 ↓	0.6 ↓	36.6 ↓	11.0 11.4 11.75	0.67 ↓	85.5 ↓	35 ↓	2.2 ↓	100% -400	8.75 6.04 5.35	TiO_2 - 9.4 Al_2O_3 - 1.1 Cu - .004 Sn - 0.14
Titanium Chemical Milling (Test No.2)	93,000 Fluoride 2.73 N Acid	4:3	80	1.5 4.0 24	- 80 70	1300 ↓	0.6 ↓	36.6 ↓	11.4 11.6 11.9	0.67 ↓	85.5 ↓	35 ↓	2.2 ↓	100% -400	2.72 1.26 0.826	TiO_2 - 9.4 Al_2O_3 - 1.1 Cu - .004 Sn - 0.14
Titanium Chemical Milling (Test No.3)	93,000 Fluoride 2.73 N Acid	4:3	80	24	70	900	0.5	36.6	12.5	1.0	85.5	35	3.7	100% -400	0.2	TiO_2 - 9.4 Al_2O_3 - 1.1 Cu - .004 Sn - 0.14
Titanium Descaling Solution 6N Acid	60,000 Fluoride 119,000 Nitrate (N)	1:1.1	100	1	140	1300	0.6	31.4	10.2	0.67	78.6	28	3.1	100% -400	0.02	TiO_2 - 3.0 Al_2O_3 - 0.6 Cu - .28 Sn - 0.5
Aluminum Deoxidizer Amchem 7-17	1400 Fluoride 126,000 Nitrate	1:0.57	50	3	72	1300	0.6	31.4	11.5	0.67	86.2	40	3.1	100% -400	0.2	TiO_2 - 0.2 Al_2O_3 - 0.6 Cu - .008 Sn - 0.02
Aluminum Conversion Coating Alodine 1200	3020 Fluoride 250 Nitrate	2.13 lbs. of Dry Ca O Per 10 Gal. Waste	10	0.5 18 21 22	80 70 70 70	1300 ↓	0.79 ↓	6.66 ↓	9.6 9.8 11.9 2.7	0.33 ↓	71.8 ↓	30.8 ↓	0.665 ↓	100% -400	16.0 11.6 10.5	TiO_2 - 2.0 Al_2O_3 - 3.0 Cu - .02 Sn - .04
Secondary Treatment On Above Effluent	10.5 Fluoride	22.9 Grams $Al_2(SO_4)_3$ Per 4 Liters		22	-	-	-	-	2.7	-	-	-	-	-	2.43	-

passed through the centrifuge as in Test No. 1. The solution was allowed to stand for four hours, after which it was mixed for one minute; an additional five gallons were then centrifuged. The remaining solution was allowed to stand for 24 hours, mixed for one minute and centrifuged. Samples of the centrifuge effluent taken at 1.5-, 4- and 24-hour retention times were analyzed and found to contain 2.72 1.26 and 0.826 parts per million of fluoride, respectively (see Table 18). The significantly lower fluoride concentrations achieved in this test as compared to those for Test No. 1 are attributed to the standing time without mixing prior to separation. The more intense mixing in test No. 1 apparently caused some redissolving of the calcium fluoride.

- Test No. 3. This test was conducted to substantiate the low fluoride concentrations achieved in Test No. 2 where the treated solution was allowed to stand prior to separation. Ten gallons of the same spent titanium chemical milling solution used in Test No's 1 and 2 were treated with 7.5 gallons of lime and allowed to stand without mixing for 24 hours. The treated solution was then mixed for one minute and passed through the centrifuge at a rate of 0.5 gallon per minute. The centrifuge effluent was analyzed and found to contain only 0.2 part per million of fluoride. This test again showed the need for solids retention without mixing to obtain a low fluoride content in the effluent.

Titanium Descaling Solution

Ten gallons of titanium descaling solution having a fluoride concentration of 60,000 parts per million and an acid concentration of 6.0 normal were treated with 11 gallons of chemical granular quicklime slurry. After treatment, the solution was allowed to stand for one hour. It was then mixed and passed through the centrifuge at a rate of 0.6 gallon per minute. The calcium fluoride sludge was skimmed out of the centrifuge bowl and physical characteristics were determined. The centrifuge effluent was analyzed and found to contain only 0.021 part per million of fluoride. Results are shown in Table 18.

Aluminum Deoxidizing Solution (2-6 Oz/Gal. Amchem 7-17, 15-20% by volume HNO_3 (42°Bé))

Ten gallons of aluminum deoxidizer were analyzed and found to contain 5500 parts per million of hexavalent chromium and 1400 parts per million of fluoride. Prior to fluoride treatment the deoxidizer solution was treated with 1.67 pounds of sodium metabisulphite which reduced the hexavalent chrome concentration to 0.055 part per million. The solution was then treated with 5.7 gallons of chemical granular quicklime slurry, allowed to stand for three hours, mixed and then passed through the centrifuge at a rate of 0.6 gallon per minute. The sludge was skimmed out of the centrifuge bowl and physical characteristics were determined. The centrifuge effluent was analyzed and found to contain 0.16 part per million of fluoride. Results are presented in Table 18.

Aluminum Conversion Coating Solution (Alodine 1200)

Ten gallons of Alodine 1200 solution obtained for treatment were analyzed and found to contain 600 parts per million of hexavalent chromium and 2020 parts per million of fluoride. Prior to fluoride treatment, the solution was treated with 157 grams of sodium metabisulfite which reduced the hexavalent chromium concentration to 0.05 part per million. The solution (10 gallons) was then treated with 2.13 pounds of dry chemical granular quicklime. The dry lime was used for treatment, because the Alodine 1200 solution has a low acid concentration and only a small amount of lime is necessary to treat the fluoride. The treated Alodine 1200 solution was mixed for ten minutes and then allowed to stand for 1/2 hour. About three gallons of the treated solution were then passed through the centrifuge at a rate of 0.79 gallon per/minute. The solution was allowed to stand for 18 hours before being mixed. An additional three gallons of solution were run through the centrifuge at a rate of 0.79 gallon per/minute. The remaining solution was allowed to stand for 21 hours before it was run through the centrifuge at a rate of 0.79 gallon per minute. Samples of the centrifuge effluents taken at the 25-minute, 18-hour and 21-hour retention times were analyzed for fluoride and found to contain 16.0, 11.6 and 10.5 parts per million of fluoride, respectively. The calcium fluoride sludge was skimmed out of the bowl and physical characteristics determined. Since an effluent having a fluoride concentration of three parts per million could not be obtained with the Alodine 1200 solution using lime treatment, a secondary treatment with aluminum sulfate to precipitate out aluminum fluoride was tried. Four liters of the centrifuge effluent from the lime treatment test were treated with 22.93 grams of aluminum sulfate.

The treated solution was mixed and allowed to stand for 22 hours. A sample of the treated solution was then removed and centrifuged for three minutes using an International Clinical centrifuge. Analysis of the clear effluent showed that the effluent had a fluoride concentration of 2.43 parts per million. Complete test results are given in Table 18.

SUMMARY OF RESULTS

The results of using calcium oxide (chemical granular quicklime) to treat four chemical processing solutions are summarized in Table 18. Test results show that titanium chemical milling solution, titanium descaling solution and aluminum deoxidizer solution can be treated to reduce fluoride effluent levels to less than one part per million using only primary treatment with lime. The fluoride concentration of the aluminum conversion coating solution (Alodine 1200) was reduced to 10.5 parts per million after primary treatment with lime. Secondary treatment of this solution with aluminum sulfate produced an effluent with less than three parts per million of fluoride.

After completion of the pilot tests, discussions were held with representatives of the Sharples Division of the Pennwalt Corporation regarding the data generated. The Sharples representatives indicated that for the solutions treated with feed solids contents greater than 30 percent, a horizontal Super-D-Canter type of centrifuge would be required (Figure 13). If a vertical basket type of centrifuge were used for production treatment, the basket would fill up so rapidly that skimming and unloading times would be too short to get a reasonably effective capacity. The calcium fluoride sludge should also be continuously unloaded, because it is too heavy to permit effective skimming.

The Super-D-Canter type of centrifuge is built to take heavy sludge and separate it while simultaneously delivering a clear effluent. Since the Super-D-Canter centrifuge utilizes a force of over 2000 times gravity, a much clearer effluent and smaller volume of drier sludge would be obtained compared to that obtained with the pilot centrifuge.

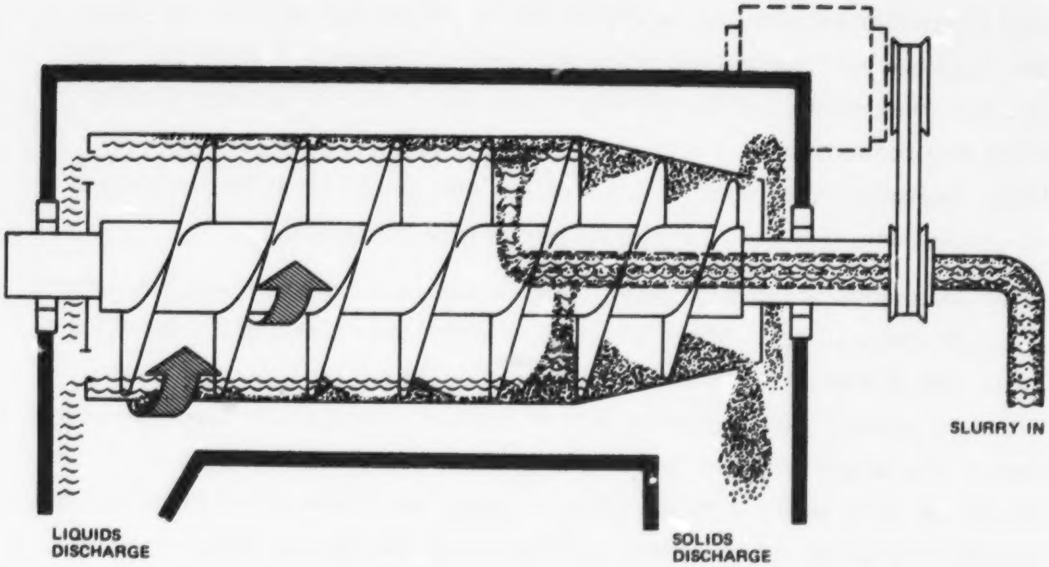
SLURRY IN
LIQUIDS DISCHARGE
SOLIDS DISCHARGE

Figure 13. Sharples Super-D-Canter Centrifuge

Based on test results obtained under this portion of the program, Grumman Aerospace Corporation rented (at no cost to the program) a Sharples P-600 Super-D-Canter centrifuge to run a production test on the 10 percent hydrofluoric acid titanium chemical milling solution. This test is described in Section VI of this report. The titanium chemical milling solution was selected for the production lime treatment test because it is the most often dumped fluoride solution used at Grumman and because it is the only one of the four solutions pilot tested which contains only fluoride as a pollutant. The other solutions that were pilot tested (titanium descaling, aluminum deoxidizer and Alodine 1200) also contain nitrates at concentrations up to 60,000 parts per million in their lime-treated effluents. In New York State nitrate concentration must be reduced to less than 10 parts per million before the effluent can be discharged. The technique for removing nitrate from these effluents is discussed in Section VI of this report and will be fully developed under Phase II of this program.

SECTION VI

ECONOMICS OF CALCIUM FLUORIDE SLUDGE RE-USE AND PRODUCTION SCALE-UP

APPROACH

This phase of the program was concerned with establishing the feasibility of re-using calcium fluoride sludge as an additive to concrete, developing a production scale-up plan and generating cost data relative to fluoride treatment. Production testing of lime treatment for 10 percent hydrofluoric acid titanium chemical milling solution was also included in this phase of the program. This test, which was not originally scheduled as part of the work for this EPA grant, is being funded by Grumman Aerospace Corporation because of the significant fluoride reduction results achieved on the titanium chemical milling solution as described in Sections IV and V of this report.

STUDY AREAS

The task of determining the economics of calcium fluoride sludge re-use and generating production scale-up data consisted of the following technical efforts:

- Evaluation of the feasibility of using calcium fluoride sludge as a concrete additive
- Evaluation of the feasibility of re-using ion-exchange rinse water effluent
- Determination of lime treatment costs for chemical process solutions
- Production scale-up plans for treatment of fluoride and nitrate-containing solution wastes
- Installation and operation of a prototype production lime treatment system for titanium chemical milling solution

EVALUATION OF CALCIUM FLUORIDE SLUDGE AS AN ADDITIVE TO CONCRETE

This test was conducted to establish the feasibility of using calcium fluoride sludge (Figure 14) from lime treatment as an additive for concrete. If the addition of calcium fluoride sludge to concrete would increase or maintain the strength of concrete, this technique would provide a means of disposing of large quantities of sludge. At the present time, most lime treatment sludges are disposed of as land fill. As land fill sites become filled and disposal regulations more stringent, however, this method will no longer be available. The problem is especially acute for companies located near large cities where land is relatively scarce.

Test Procedure

Tests were conducted on concrete prepared using procedures of ASTM Standards C 109-70T and C 305. The compositions of the concrete specimens tested were as follows:

- Mixture No. 1 (Standard Mixture)
  - 250 grams of Type I Portland Cement
  - 687.5 grams of sand, graded as per ASTM Standard C 109
- Mixture No. 2 (Standard Mix Plus Extra Sludge)
  - 250 grams of Type I Portland Cement
  - 687.5 grams of sand, graded as per ASTM Standard C 109
  - 757 grams of wet titanium descaling solution sludge from previous pilot centrifuge tests - (100 grams as dry sludge)
- Mixture No. 3
  - 250 grams of Type I Portland Cement
  - 623 grams of sand, graded as per ASTM Standard C 109
  - 230 grams of wet titanium descaling solution sludge from previous pilot centrifuge tests (64.5 grams as dry sludge)

The standard mixture as well as the mixtures containing sludge (Table 19) were prepared using procedures outlined in ASTM Standard C305. Three 1.575 x 1.575 x 6.3-inch flexural specimens were cast from each mixture (Figure 15).

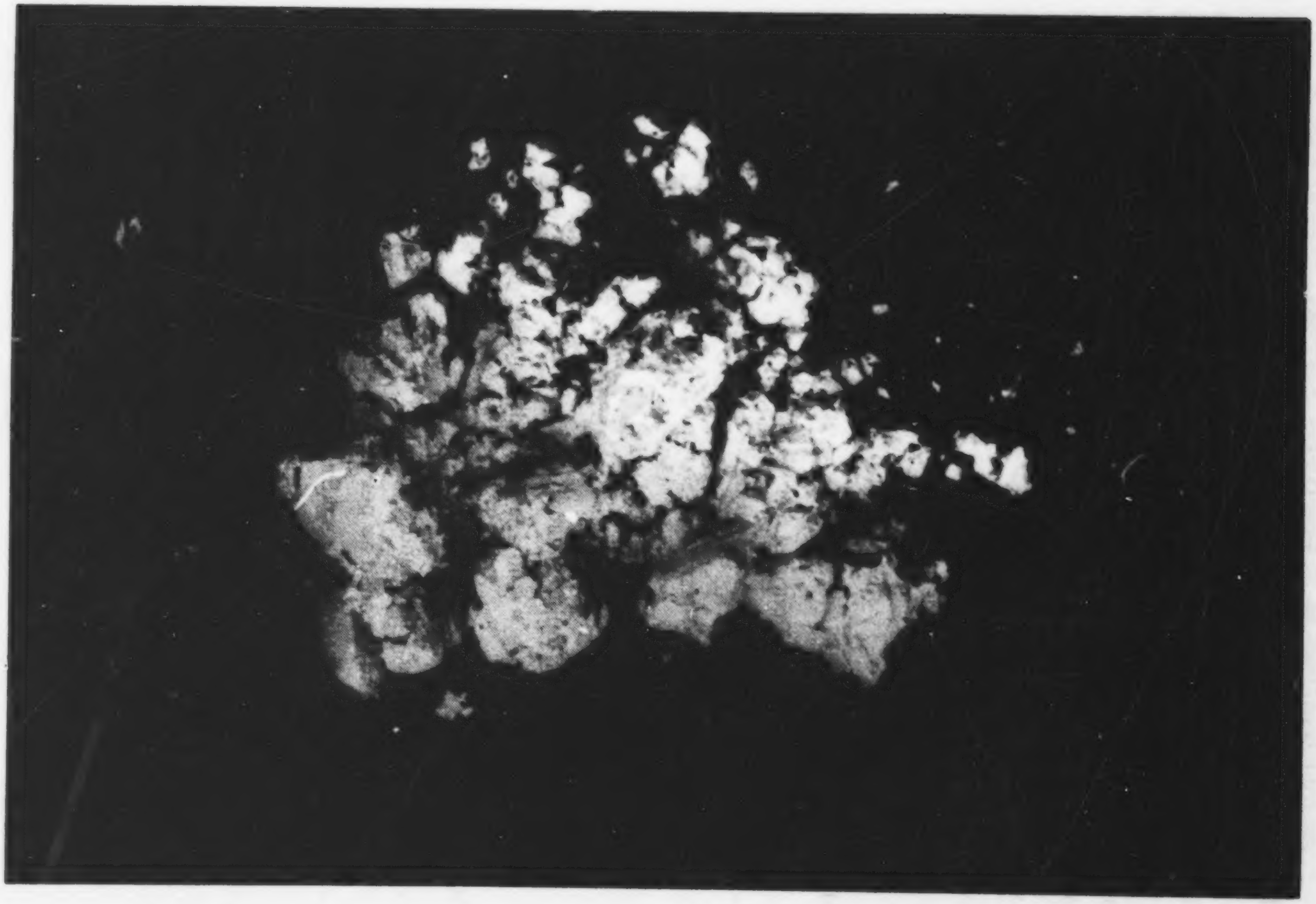

Figure 14. Calcium Fluoride Sludge from Lime Treatment of Titanium Chemical Milling Solution

TABLE 19 FLEXURAL AND COMPRESSIVE STRENGTH TEST RESULTS

FOR REGULAR AND SLUDGE-CONTAINING CONCRETES

Mixture No.	Ratio of Cement To Solids	Percentage of Cement (%)	Percentage of Sand (%)	Percentage of Sludge (%)	Flexural Test No.	Beam Depth (in)	Beam Width (in)	Fail Load (pounds)	Flexural Strength (psi)	Average Flexural Strength (psi)	Compressive Test No.	Sample Height (in)	Area of Sample (in^2)	Maximum Load (pounds)	Compressive Strength (psi)	Average Compressive Strength (psi)
1	1:2.75	26.7	73.3	0	1 2 3	1.581 1.580 1.576	1.535 1.551 1.543	315 311 298	567 560 536	554	1-1 1-2 2-1 2-2 3-1 3-2	1.582 1.582 1.579 1.578 1.577 1.577	2.319 2.333 2.334 2.369 2.316 2.321	5590 5825 5200 5160 5080 5740	2410 2495 2230 2180 2195 2475	2330
2	1:3.16	24.1	66.4	9.5	1 2 3	1.577 1.572 1.578	1.565 1.568 1.561	204 224 216	357 404 389	383	1-1 1-2 2-1 2-2 3-1 3-2	1.579 1.579 1.572 1.571 1.580 1.580	2.503 2.490 2.493 2.484 2.482 2.488	4300 4220 4025 4000 4475 4450	1715 1695 1615 1610 1805 1790	1705
3	1:2.75	26.7	66.5	6.8	1 2 3	1.561 1.571 1.572	1.538 1.526 1.537	290 298 329	522 536 592	550	1-1 1-2 2-1 2-2 3-1 3-2	1.564 1.568 1.573 1.575 1.576 1.576	2.402 2.420 2.421 2.462 2.457 2.390	6280 7280 7190 7200 6900 7280	2615 3010 2970 2925 2810 3045	2895

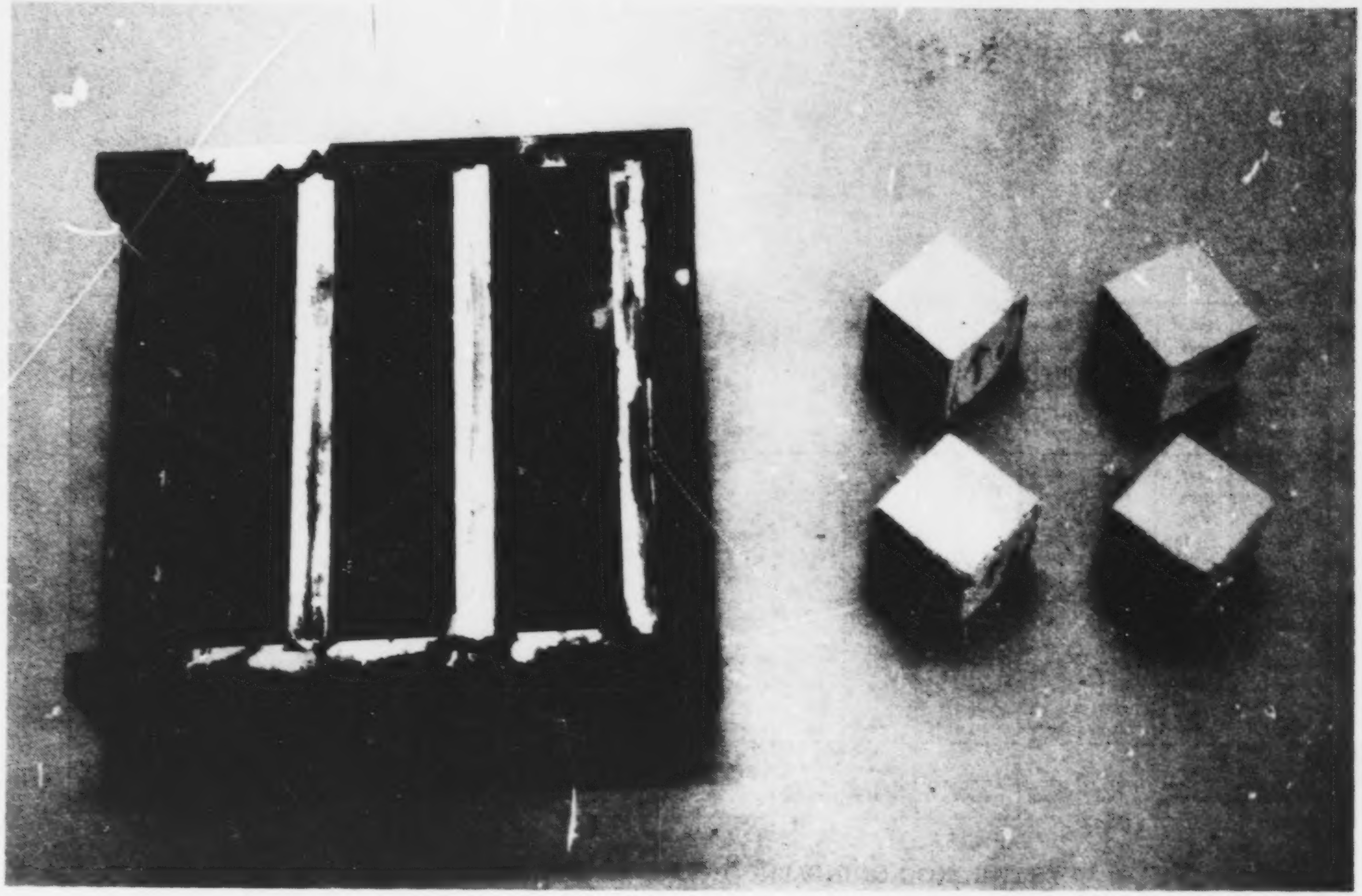

Figure 15. Mold for Casting Concrete-Calcium Fluoride Sludge Flexural Strength Test Specimens and Cubical Compressive Strength Test Specimens

The specimens were cured for seven days at 90 percent relative humidity and at a temperature of 23°C± 1.7°C per ASTM Standard C 109. The cured flexural strength specimens were tested per ASTM Standard C 348 on a Wiedemann Baldwin 30B, 30,000-pound universal testing machine (Figure 16). After testing, the flexural strength specimens were cut into cubical compression strength specimens using a diamond saw blade and tested per ASTM Standard C 116 on a Wiedemann Baldwin 30B universal testing machine in (Figure 17).

Test Results

Flexural and compressive strength test results for the three mixtures evaluated are shown in Table 19. The compressive strength of Mixture No. 3, which contains 6.8 percent sludge (cement-to-solids ratio of 1:2.75), is higher than that for standard concrete (Mixture No. 1). The flexural strength of Mixture No. 3 was about equivalent to that for standard concrete. The compressive and flexural strength values for Mixture No. 2, which contains 9.5 percent sludge, (cement-to-solids ratio of 1:3.16) are lower than those for standard concrete. These results show that it is potentially feasible to use calcium fluoride sludge as an additive to concrete.

LEACHABILITY OF SLUDGE CONCRETE

A leachability test was conducted to determine if concrete containing calcium fluoride sludge would lose fluorides when continuously exposed to running water. In this test, 45 ounces of sludge concrete Mixture No. 2 were subjected to continuous recirculation of two liters of tap water for a period of two weeks (Figure 18). The water was checked for fluoride content, pH and conductivity before and after the test. Initial values were a pH of 5.9, a conductivity of 46 micromhos per centimeter and a flouride content of 0.068 part per million. After two weeks of continuous recirculation, the water had a pH of 11.1, a conductivity of 10,300 micromhos per centimeter and a fluoride level of 1.7 parts per million. This test showed that an insignificant amount of fluorides is leached out of sludge concrete. The rise in pH and conductivity is due mainly to other leachable materials in the concrete (e.g., lime). Based on the results of the flexural and compressive strength tests as well as the results of the leachability test, further development work to establish sludge concrete as a viable material for roads will be performed under Phase II of this program.

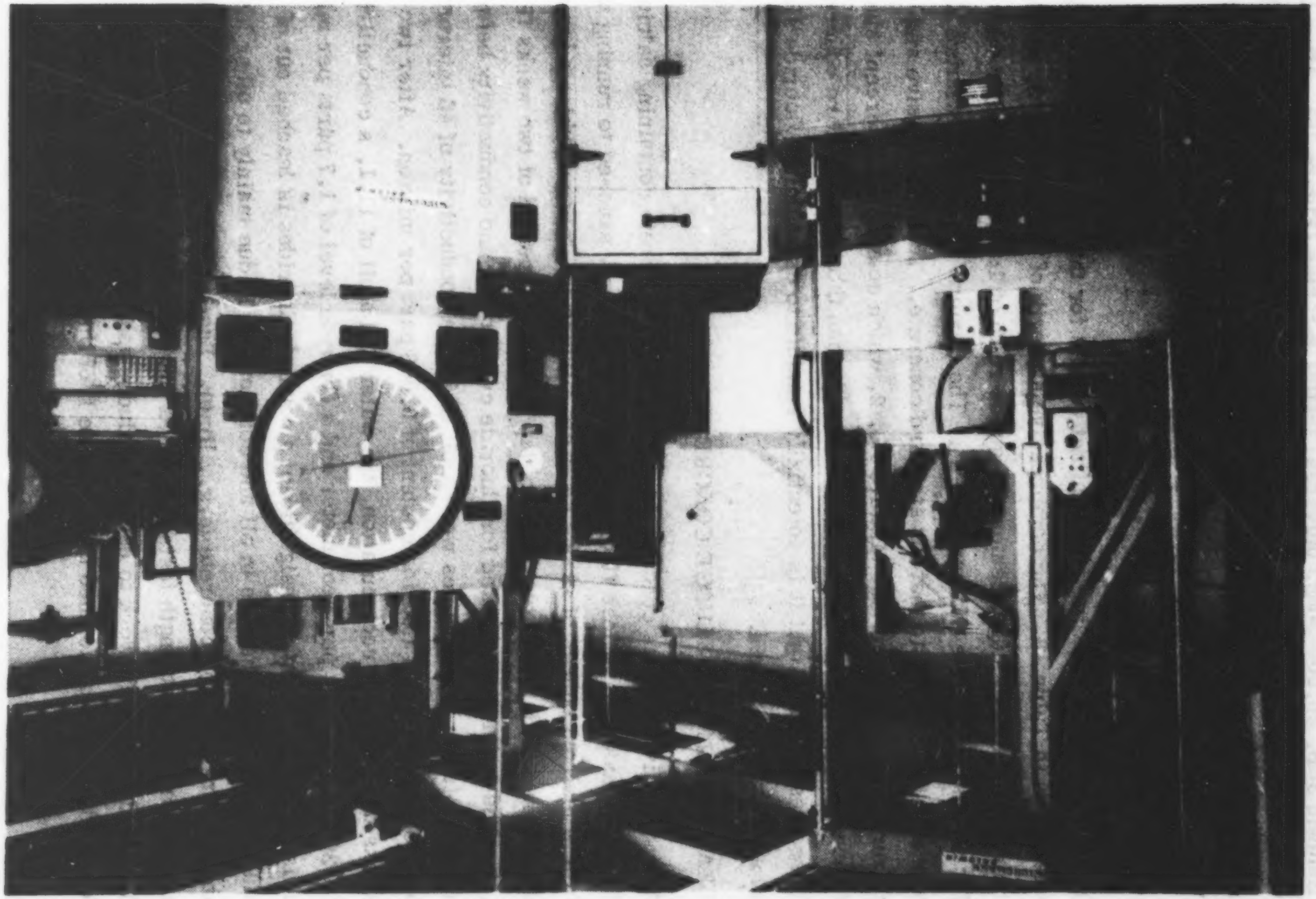

Figure 16. Wiedemann Baldwin 30B, 30,000-Pound Universal Testing Machine

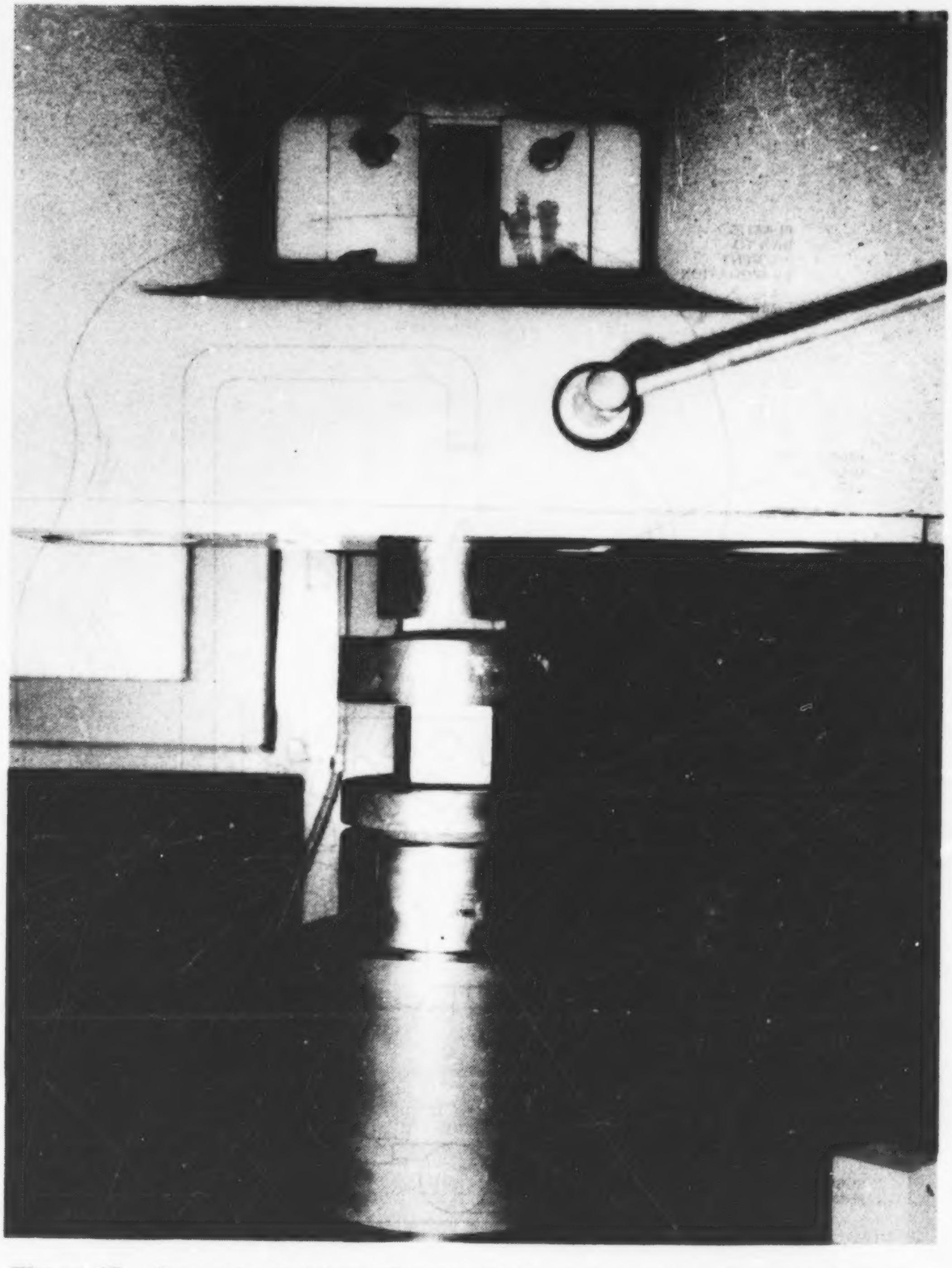

Figure 17. Concrete-Calcium Fluoride Sludge Compression Strength Specimen Being Tested in Wiedemann-Baldwin 30B Universal Testing Machine

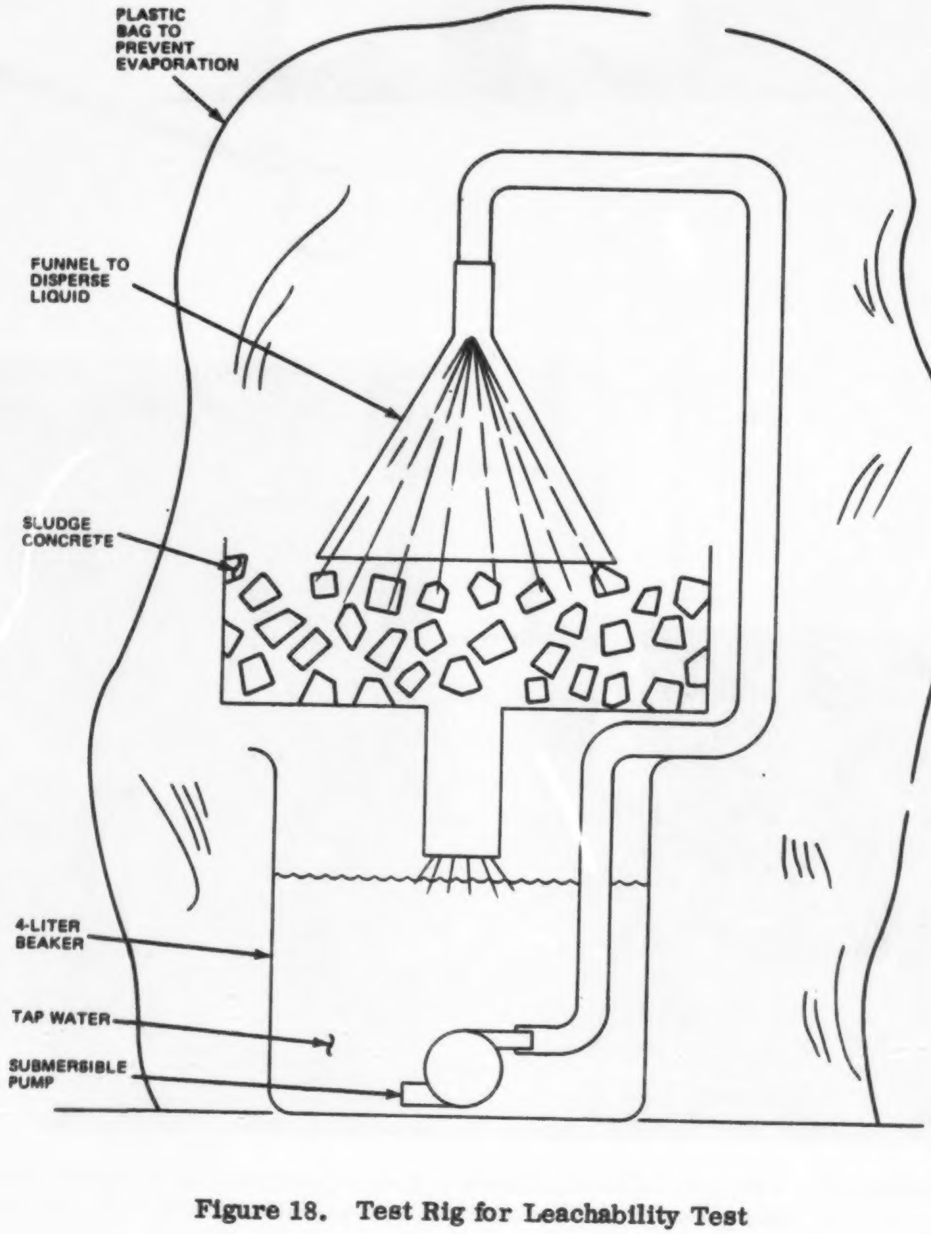
PLASTIC BAG TO PREVENT EVAPORATION
FUNNEL TO DISPERSE LIQUID
SLUDGE CONCRETE
4-LITER BEAKER
TAP WATER
SUBMERSIBLE PUMP

Figure 18. Test Rig for Leachability Test

RE-USE OF ION-EXCHANGE RINSE WATER EFFLUENT

Re-use of the effluent liquids from ion-exchange columns as rinse water or solution make-up water would eliminate the need for ground water disposal of these liquids. Two important analytical characteristics that affect rinse water re-use are pH (a measure of acidity) and specific conductance (a measure of a fluid's capacity to convey an electric current). Since the specific conductance is affected by the nature and concentration of the substances dissolved in a fluid, it gives an indication of the degree of purity of that fluid.

The total flow of rinse water for the titanium chemical milling solution is 10,000 gallons for 16 hours use. Results obtained for this solution using the series ion-exchange system described in Section IV showed that the solution can be re-used. The pH, conductivity and fluoride concentration ranges for titanium chemical milling rinse water before and after ion-exchange treatment were as follows:

PARAMETER	INFLUENT	EFFLUENT
pH	2-4	3-5
Conductivity (micromhos/centimeter)	120-2000	60-600
Fluoride Concentration (ppm)	3-60	1-2

LIME TREATMENT COSTS FOR CHEMICAL PROCESS SOLUTIONS

The cost to treat waste titanium chemical milling, titanium descaling and aluminum deoxidizing solutions with lime was calculated using the following equation:

$$C_t = (V_s/V_c)\,(D_s)\,(C_l)\,(V_k)$$

where C_t = cost to lime treat waste solution, \$

V_s/V_c = ratio of lime slurry, to waste solution

D_s = lime slurry concentration, 2.03 lbs/gal

C_l = lime cost, \$0.0105/lb

V_k = total volume of waste solution to be treated, gal

The lime slurry/waste solution ratios used for titanium chemical milling, titanium descaling and aluminum deoxidizing solutions were 3/4, 1.1/1.0 and 0.57/1.0, respectively. The lime treatment costs per 1,000 gallons of solution are as follows:

- Titanium Chemical Milling Solution - $ 15.97
- Titanium Descaling Solution - $ 23.41
- Aluminum Deoxidizing Solution - $ 12.12

The cost to treat waste aluminum conversion coating solution (Alodine 1200) consists of both the primary treatment cost with lime and the secondary treatment cost with aluminum sulfate. These costs were calculated using the following equation:

$$C_t = (W)(C)(V)$$

where C_t = cost to treat waste solution, $

W = weight of treatment material, lbs/gal of waste solution (0.213 lb of lime or 0.0478 lb of aluminum sulfate)

C = cost of treatment material, $0.0105/lb for lime and $0.035/lb for aluminum sulfate

V = total volume of waste solution to be treated, gal

Primary (lime) and secondary (aluminum sulfate) treatment costs per 1,000 gallons of waste aluminum conversion coating solution are $2.23 and $1.67, respectively. Total treatment cost for this solution is $3.90 per 1,000 gallons.

The calculated costs pertain only to the treatment of waste chemical process solutions to remove fluorides. The calcium fluoride sludge produced must either be carted away to land-fill sites or be re-used in other applications (e.g., sludge concrete). Although the cost of dumping calcium fluoride sludge is relatively low, the precise cost depends on the geographic location and availability of the land-fill sites. Land disposal of calcium fluoride sludge, however, has the potential for causing problems because of its relatively high solubility, particularly where the ground water is used for drinking water supplies.

PRODUCTION SCALE-UP PLANS FOR TREATMENT OF PROCESS SOLUTIONS AND RINSE WATERS

Treatment of Process Solutions

A proposed layout of a production installation to treat fluoride and nitrate-containing process solutions is shown in Figure 19. The system would utilize a centrifuge for separation and removal of precipitated fluorides and a mechanically

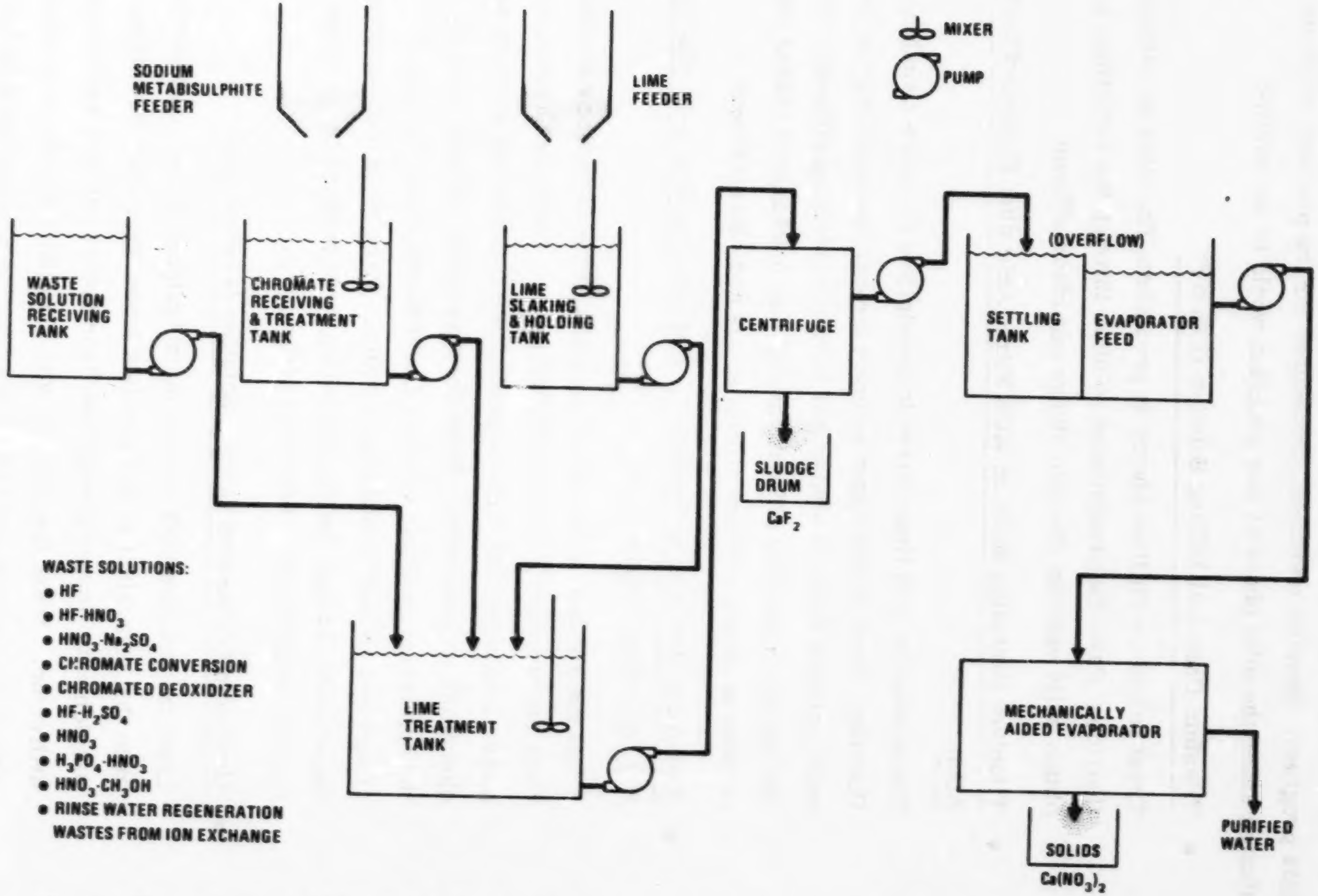
SODIUM METABISULPHITE FEEDER
LIME FEEDER
MIXER
PUMP
WASTE SOLUTION RECEIVING TANK
CHROMATE RECEIVING & TREATMENT TANK
LIME SLAKING & HOLDING TANK
CENTRIFUGE
(OVERFLOW)
SETTLING TANK
EVAPORATOR FEED
SLUDGE DRUM
CaF_2
WASTE SOLUTIONS:
• HF
• $HF\text{-}HNO_3$
• $HNO_3\text{-}Na_2SO_4$
• CHROMATE CONVERSION
• CHROMATED DEOXIDIZER
• $HF\text{-}H_2SO_4$
• HNO_3
• $H_3PO_4\text{-}HNO_3$
• $HNO_3\text{-}CH_3OH$
• RINSE WATER REGENERATION WASTES FROM ION EXCHANGE
LIME TREATMENT TANK
MECHANICALLY AIDED EVAPORATOR
SOLIDS
$Ca(NO_3)_2$
PURIFIED WATER

Figure 19. Proposed Industrial Waste Treatment Facility for Fluorides, Nitrates and Chromates

aided evaporator for removal of nitrates from the centrifuge effluents. The parameters for operation of the evaporator will be established under Phase II of this program. Specific treatment procedures for the process solutions evaluated under the pilot phase of this program would be as follows:

- Titanium Chemical Milling Solution (10% HF)

  Treat solution with lime slurry to precipitate fluorides as calcium fluoride. Pass the precipitated solution through the centrifuge to obtain solid calcium fluoride sludge and clear effluent.

- Titanium Descaling Solution (40% Nitric Acid plus 2% Hydrofluoric Acid)

  Treat solution with lime slurry to precipitate fluorides as calcium fluoride. Pass precipitated solution through the centrifuge to obtain solid calcium fluoride sludge and nitrate-containing effluent. Pass the nitrate-containing effluent through the mechanically aided evaporator to obtain calcium nitrate solids and clear effluent.

- Aluminum Deoxidizing Solution (2-6 oz/gal Amchem 7-17 plus 15%-20% by volume Nitric Acid)

  Treat the solution with sodium metabisulphite to reduce chromium from the hexavalent to the trivalent form. Treat the chromium-reduced solution with lime to precipitate fluorides as calcium and chromium as hydroxide. Pass the precipitate solution through the centrifuge to obtain calcium fluoride-chromium hydroxide sludge and effluent containing nitrates. Pass the nitrate-containing effluent through the mechanically aided evaporator to obtain calcium nitrate solids and clear effluent

- Aluminum Conversion Coating Solution (Alodine 1200)

  Treat the solution with sodium metabisulphite to reduce chromium from the hexavalent to the trivalent from. Treat the chromium-reduced solution with lime to precipitate fluorides as calcium and chromium as hydroxide. Treat the solution with aluminum sulfate to precipitate aluminum fluoride and reduce the fluoride concentration to less than three parts million. Pass the precipitated solution through the centrifuge to obtain calcium fluoride-chromium hydroxide-aluminum

> fluoride sludge and effluent containing nitrates. Pass the nitrate-containing effuent through the mechanically aided evaporator to obtain calcium nitrate solids and clear effluent.

Treatment of Rinse Waters

A proposed layout of a production installation to treat fluoride and nitrate-containing rinse waters is shown in Figure 20. This captive rinse system would utilize Rohm & Haas Amberlite IRA 400 resin for fluoride removal and Alcoa F-1 activated alumina for fluoride removal and pH adjustment. The sodium hydroxide regeneration waste from the IRA 400 resin and the sulfuric acid regeneration waste from the activated alumina would be passed back to the lime treatment tank shown in Figure 19, and treated as follows:

> Treat the regeneration wastes with lime slurry to precipitate fluorides as calcium fluoride. Pass the precipitated solution through the centrifuge to obtain solid calcium fluoride sludge and effluent containing nitrates. Pass the nitrate-containing effluent through the mechanically aided evaporator to obtain calcium nitrate solids and clear effluent.

INSTALLATION AND OPERATION OF PROTOTYPE PRODUCTION LIME TREATMENT SYSTEM FOR TITANIUM CHEMICAL MILLING SOLUTION

Objective

The objective of this study was to demonstrate on a pilot-line basis the effectiveness of the lime treatment technique for fluoride waste disposal. Specific goals were:

- Treatment of spent titanium chemical milling solution with lime to reduce fluoride concentration to three ppm or less
- Separation of reaction solids (calcium fluoride and metal oxides) from the treated solution using centrifugal/settling tank procedures

Treatment Procedure

The recommended procedure for treating titanium chemical milling solution is as follows:

- Lime Slaking. Prepare calcium hydroxide slurry by adding 2.03 pounds of chemical granular quicklime per gallon of water

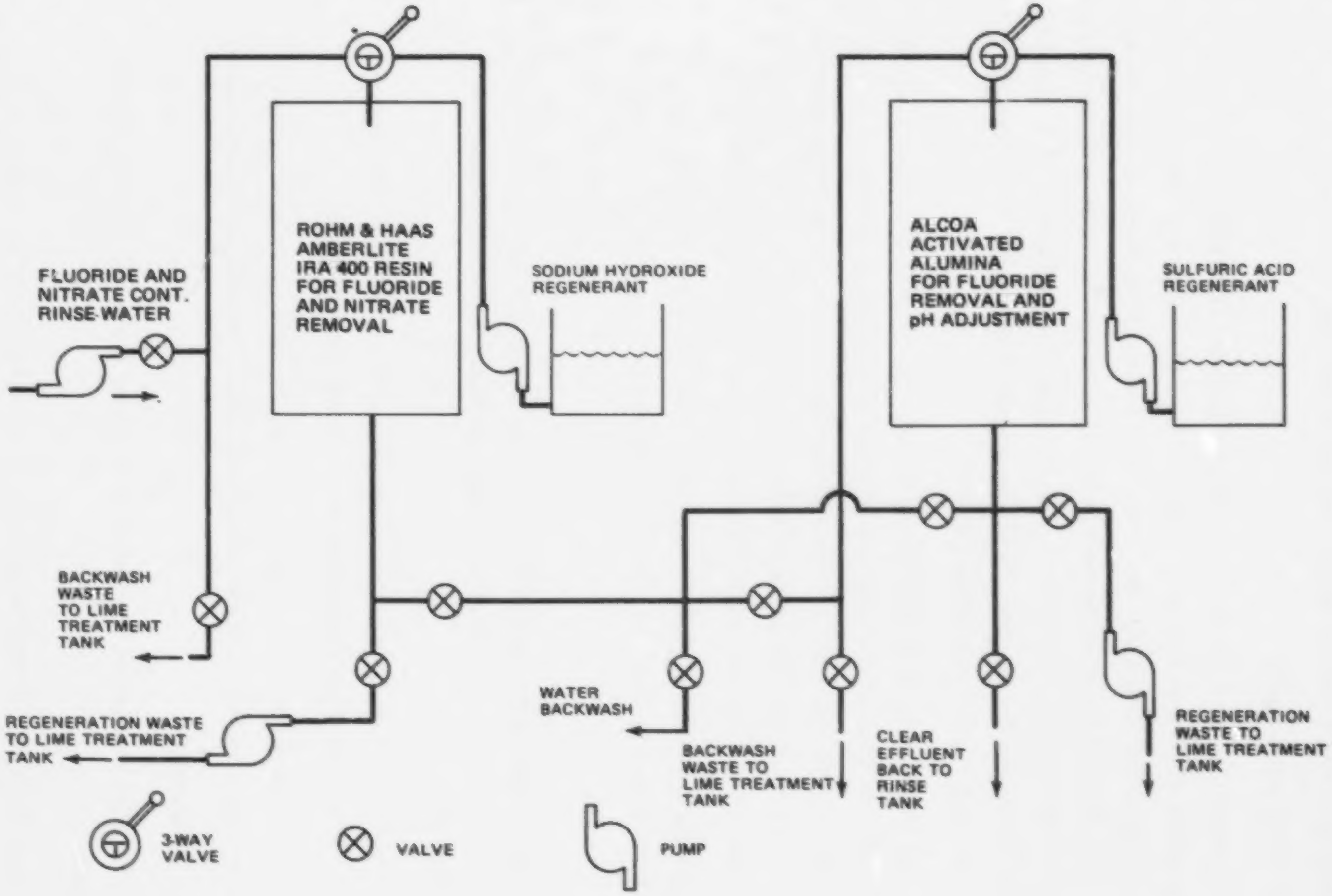
FLUORIDE AND NITRATE CONT. RINSE WATER
ROHM & HAAS AMBERLITE IRA 400 RESIN FOR FLUORIDE AND NITRATE REMOVAL
SODIUM HYDROXIDE REGENERANT
ALCOA ACTIVATED ALUMINA FOR FLUORIDE REMOVAL AND pH ADJUSTMENT
SULFURIC ACID REGENERANT
BACKWASH WASTE TO LIME TREATMENT TANK
REGENERATION WASTE TO LIME TREATMENT TANK
WATER BACKWASH
BACKWASH WASTE TO LIME TREATMENT TANK
CLEAR EFFLUENT BACK TO RINSE TANK
REGENERATION WASTE TO LIME TREATMENT TANK
3-WAY VALVE
VALVE
PUMP

Figure 20. Proposed Ion-Exchange System for Fluoride and Nitrate-Containing Rinse Waters

- Fluoride Solution Treatment. Add three parts by volume of calcium hydroxide slurry to four parts by volume of titanium chemical milling solution. Mix the reactants thoroughly while adding the slurry.
- pH Adjustment. The pH of the treated solution should be between 11.0 and 12.5 for optimum results. If necessary, adjust the pH by adding calcium hydroxide slurry.
- Solids Retention. After adding the calcium hydroxide slurry, allow the treated solution to stand unagitated for at least 24 hours.
- Centrifugal Separation. Centrifuge the treated solution to provide effluent and calcium fluoride sludge.
- Settling Tank Separation. Discharge the effluent into a holding/settling tank and allow it to stand unagitated for at least 32 hours to permit settling of the particles not separated by the centrifuge. At the end of this period, the supernatant liquid is ready for discharge into leaching ponds.
- Sludge Removal. The solid material obtained from the centrifugal separation operation does not require further treatment.

Process Demonstration

Based on the data generated during the course of this grant, the recommended procedure described previously was evaluated using 1,000 gallons of spent titanium chemical milling solution.

- Lime Slaking (Figure 21)
  - 900 gallons of water were added to the lime storage tank (No. 779)
  - 1,840 pounds of Pfizer chemical granular quicklime were added to the three lime holding drums located above the lime tank
  - The quicklime was slaked by rapidly adding it to the 900 gallons of water in Lime Tank No. 779 and continuously agitating the slurry by mechanical stirring. The slurry reached a maximum temperature of 220°F about 20 minutes after addition of the quicklime.

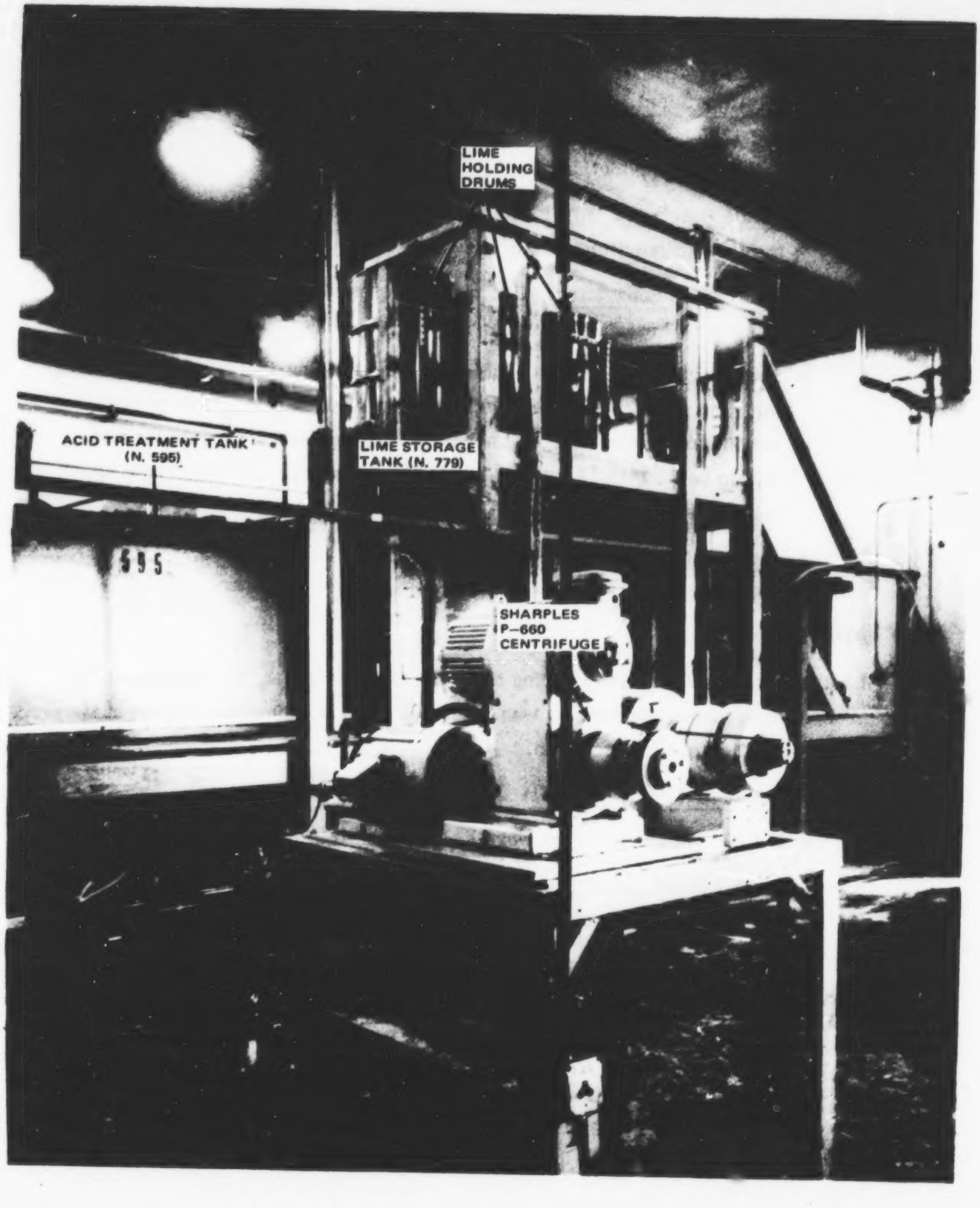
LIME HOLDING DRUMS
ACID TREATMENT TANK (N. 595)
LIME STORAGE TANK (N. 779)
595
SHARPLES P-660 CENTRIFUGE

Figure 21. Pilot-Line Lime Treatment System

- The lime slurry was continuously stirred over a three to four-day period. Probe inspection showed the presence of clumps of unsuspended lime in the corners of the tank due to inefficient agitation in the square corners of the tank. The lime clumps were broken up by directing compressed air against them. This brought about suspension of the lime.

- Fluoride Solution Treatment. 750 gallons of lime slurry were added to 1,000 gallons of spent hydrofluoric acid (87,700 ppm fluoride) in the acid treatment tank (No. 595). The lime slurry was pumped into the acid treatment tank at a rate of about 18 gallons per minute. The temperature of the spent solution rose to 170°F.

- pH Adjustment. The pH of the treated spent acid was 10.3. Mechanical breakdown of the slurry pump prevented adjustment of the pH from the recorded value of 10.3 to the recommended 11.0-12.5 range.

- Solids Retention. Since the temperature of the treated solution (170°F) was high enough to possibly damage the polyvinyl chloride (PVC) tank liner, the treated solution was agitated for about 18 hours to dissipate the heat of reaction and reduce the solution temperature to about 120°F. This prevented damage to the PVC liner. The solution was allowed to remain unagitated for four hours before the solution was analyzed to determine the total fluoride concentration. The total fluoride concentration was 3 ppm.

  In previous laboratory studies using the recommended procedure, fluoride concentrations as low as 0.2 ppm were obtained in the treated solution. Departures from the recommended method (incomplete suspension of the lime slurry, lack of pH adjustment and reduced solids retention time) resulted in higher fluoride concentrations for the pilot-line treatment process. Reduction of the fluoride concentration to the goal value of 3 ppm in spite of the above process variations demonstrated the suitability of the treatment process for production use.

- Centrifugal Separation. The solids were separated from the treated acid solution with a Sharples P-660 Super-D-Canter centrifuge

(Figure 22). This unit, which was rented from the Pennwalt Company of Warminster, Pennsylvania, was used in conjunction with a variable-speed feed pump that transferred the treated solution from the reaction tank to the centrifuge feed tube. An auxiliary feed line was connected to the centrifuge system to permit the addition of flocculants (chemical agents that cause particle aggregation) to the treated solution. The flocculating agents were transferred to the centrifuge from a 55-gallon drum by a chemical feed pump. The separated solids (calcium fluoride sludge) were collected in a drum located under the centrifuge. The centrate was pumped to a holding tank.

Centrifugal separation was accomplished at a speed of 6,200 rpm. The 2,900-rpm pinion speed (rear drive) and No. 4 pond setting (position of the centrate discharge plate for separation refinement) were in accordance with the manufacturer's recommendations. Separations were conducted at various feed rates with and without the addition of polyelectrolyte flocculants. The two flocculants evaluated were Hercofloc 812.3 (cationic agent) manufactured by Hercules Incorporated, Wilmington, Delaware, and Aquafloc 423 (anionic agent) manufactured by the Dearborn Chemical Division of the Chemed Corporation, Lake Zurich, Illinois.

The results of the separation tests are summarized in Table 20. In Separations 1 and 2, the treated solution was passed through the centrifuge at rates of 0.58 and 2.16 gpm, respectively. Analysis of the centrifuge effluent showed that the effluent had a fluoride concentration between 3 and 4 ppm. The amount of solids removed (based on an initial solids concentration of 177,500 ppm) was 95.04 percent. The effluent from Test No. 2 was allowed to settle for 32 hours and was again analyzed for suspended solids concentration. The analysis showed that 99.99 percent of the solids was removed from the effluent. During Separations 3 through 6, Hercofloc 812.3 flocculant was added to the feed stream in an attempt to reduce the amount of suspended solids. Comparison of the test results with those for Test No. 2 shows that about four percent more solids were removed while the fluoride concentration remained at 3 ppm. Although addition of the

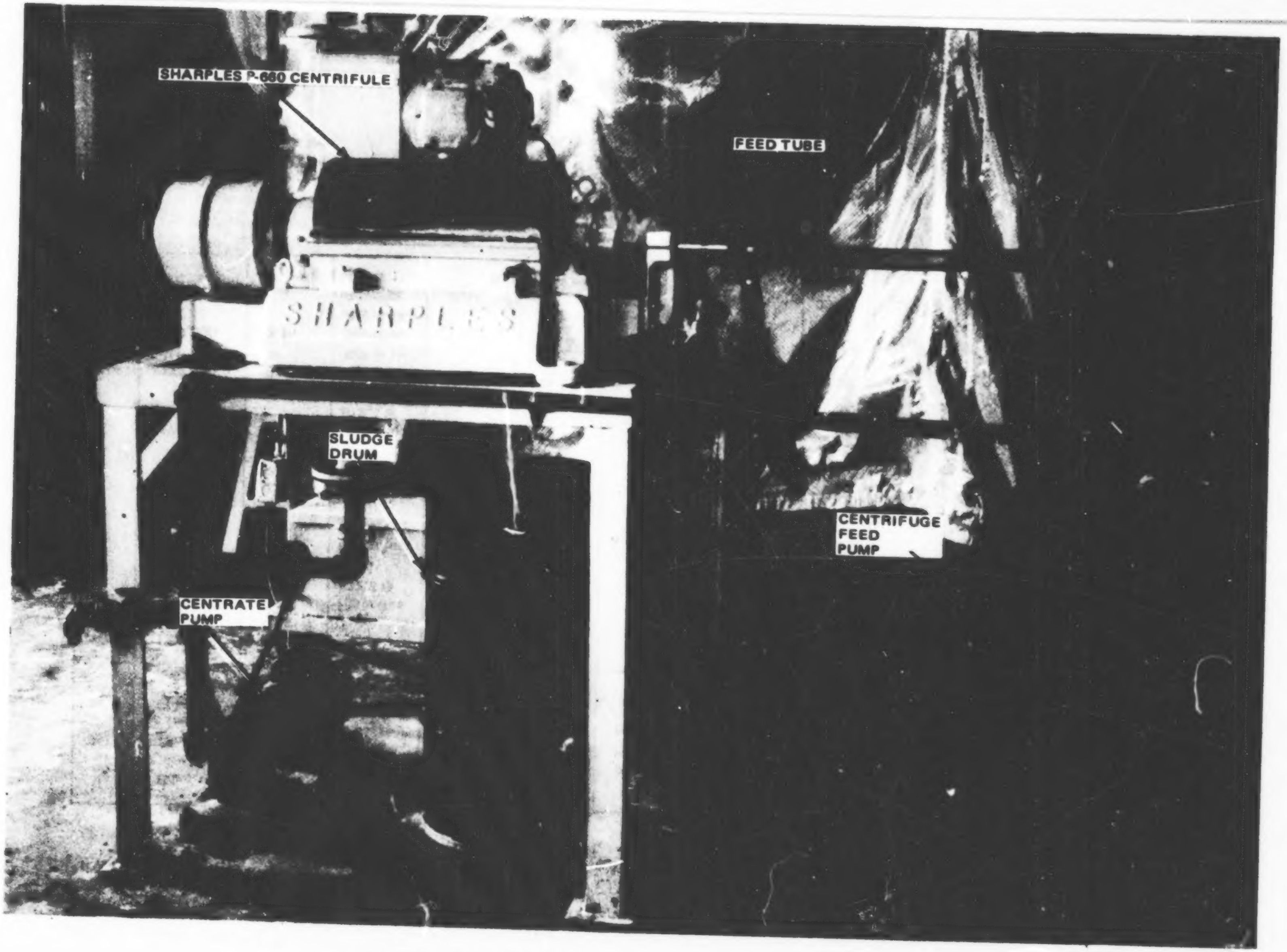
SHARPLES P-660 CENTRIFULE
SHARPLES
FEED TUBE
SLUDGE
DRUM
CENTRIFUGE
FEED
PUMP
CENTRATE
PUMP

Figure 22. Centrifugal Separation System

TABLE 20

RESULTS FOR CONTRIFUGAL SEPARATION OF TREATED TITANIUM CHEMICAL MILLING SOLUTION

Test No.	Conc. of Suspended Solids Initial (ppm)	Centrifuge Feed Rate (gal/min.)	Polyelectrolyte (%)	Polyelectrolyte Feed Rate (gal/min.)	pH of Effluent	Fluoride Conc. of Effluent (ppm)	Conc. of Suspended Solids in Effluent (ppm)	Solids Removal (%)	Conc. of Dissolved Solids in Effluent (ppm)	Conc. of Suspended Solids After 32 Hrs (ppm)	Solids Removal in Settled Effluent (%)	Sludge in Solids (%)
1	177,500	0.58	–	–	10.4	4	5280	97.04	464	–	–	48
2	177,500	2.16	–	–	10.4	3	8800	95.04	–	18	99.99	48
3	177,500	2.16	Hercofloc 812.3 @ 1/2%	0.22	10.4	4*	1330	99.25	–	–	–	57
4	177,500	2.16	Hercofloc 812.3 @ 1%	0.13	10.4	3	1860	98.95	–	–	–	–
5	177,500	2.16	Hercofloc 812.3 @ 1/2%	0.37	10.4	3	1210	99.32	–	–	–	–
6	177,500	2.16	Hercofloc 812.3 @ 1%	0.22	10.4	3	1290	99.27	–	–	–	–
7	177,500	0.58	Aquafloc 423 @ 1%	0.07	10.4	12	10	99.99	814	–	–	61
8	177,500	2.16	Aquafloc 423 @ 1%	0.168	10.4	9	231	99.87	480	–	–	63
9	177,500	1.2	Aquafloc 423 @ 1%	0.07	10.4	19	16	99.99	278	–	–	61

*Sharples P-660 Centrifuge
Bowl Speed - 6200 rpm
Pinion Speed - 2900 rpm
Pond Setting - No. 4

polyelectrolyte flocculant improved the efficiency of the centrifugal separation, the resultant effluent was cloudy and would not clear up after standing. In Separations 7, 8 and 9, Aquafloc 423 polyelectrolyte flocculant was evaluated. This flocculant gave high solids removal values (99.87 to 99.99 percent). Analysis of the effluent, however, showed that the fluoride concentration had increased to between 9 and 19 ppm. This anionic flocculant apparently reduced the concentration of the free calcium ion, thereby permitting additional calcium fluoride to dissolve and increase the fluoride ion concentration.

- Sludge Analysis. Analysis of a sludge sample by optical emission spectroscopy gave the following results:

Element	Percent
Calcium	>10
Titanium	>10
Aluminum	1
Vanadium	1
Tin	0.10
Copper	0.02
Iron	0.10
Silicon	0.05

The sludge consists mainly of calcium fluoride and metal oxides of titanium, aluminum and vanadium. This type of material is routinely sent to land fill sites for disposal.

Cost Studies for Prototype System

- Equipment. The estimated equipment requirements for a production, fluoride-treatment system for chemical processing solutions are as follows:
  - Lime Slaking System (500 tons per year). This would include a camlock valve, piping, bin vent, bin level indicator, 50-ton capacity storage silo, discharge valve, screw conveyor, slaking tank, sonic

probes, slaking pump, flow meters, solenoids, three-way port valve and storage tank. This system would cost about $20,000.

  - Centrifugal Separation System. A system consisting of a Sharples Model P-3400 stainless steel centrifuge capable of handling 20 to 30 gallons per minute of treated chemical milling solution and a 10,000-gallon settling tank would cost about $40,000

- **Chemicals.** The cost of chemical granular quicklime ($21 per ton) to treat 6,000 gallons of spent titanium chemical milling solution would be $95.91. If a polyelectrolyte flocculant were used, the cost would be about $90.00 for 6,000 gallons of spent titanium chemical milling solution. This cost is based on the use of a one-percent solution of flocculant at a feed rate of 0.1 gallon per minute.

Section VII

BIBLIOGRAPHY

1. Beckman Technical Data Sheet No. 1735-A, "Fluoride Ion Electrode," Beckman Instruments, Inc., Scientific Instruments Division, Fullerton, California 92634, November 1968

2. Boruff, C.S., et al, "Adsorption of Fluoride from Salts by Alum Floc," Industrial and Engineering Chemistry, Volume 28, No. 10

3. De Moura, J., "Specific Ion Electrodes Used to Study Interactions of Glucose -1- Phosphate and Mg^{++} and F^-," Arch. Biochem. Biophys, University of Idaho, Moscow, Idaho, 134 (1), 258-9, 1969

4. Halbedel, H.S., "Acid Fluorides and Safety," Technical Sheet No. 768, The Harshaw Chemical Company, 1971

5. Handbook of Physics and Chemistry, The Chemical Rubber Company, 45th Ed, p. B-147

6. Kolthoff, I.M. and Sandell, E.B., Textbook of Quantitative Inorganic Analysis, 3rd Ed., p. 58

7. Kuzyakin, E.B., et al, "Relationship of the Settling Rate of Waste Water Precipitants to the Ionic Composition during their Defluorination with Lime, Aluminum Sulfate, and Polyacrylamide."

8. Mac Intire, W.H., et al, "Removal of Fluorides from Natural Waters by Calcium Phosphates," Industrial and Engineering Chemistry, Vol. 30, No. 2.

9. Ockershausen, R.W., "Disposal of Hydrofluoric Acid Wastes," Industrial Chemicals Division, Allied Chemical Corporation.

10. Vanderborgh, N.E., "Evaluation of the Lanthanum Fluoride Membrane Electrode Response in Acidic Solutions," Talanta, Vol. 15, p. 1009-1013, 1968

11. Warner, T.B., "Lanthanum Fluoride Electrode Response in Water and 1M Sodium Chloride," U. S. Government Research and Development Report 69(17)-68, Naval Research Laboratory, Washington. D.C., 1969

Report 69(17)-68, Naval Research Laboratory, Washington, D. C., 1969

12. Zabban, W., and Jewett, H. W., "The Treatment of Fluoride Wastes," Water and Sewage Works, p. 415, November 1967

13. Instruction Manual, Fluoride Ion Activity, Electrode Model 94-09, Orion Research Incorporated, Cambridge, Massachusetts

14. Chemical Engineer's Handbook, Perry's John H, Fourth Edition, 1963

15. Rohm and Haas Technical Bulletin 1E-73-63, Helpful Hints in Ion Exchange Technology

16. Chemical Lime Facts, Bulletin 214, National Lime Association, Washington, D.C 20005

Section VIII

APPENDIX

FLUORIDE ANALYSIS PROCEDURE

Sample Make-Up Mixtures

Process Solution

1 ml process solution
100 ml distilled water (exact volumes are necessary)
10 ml 0.1M disodium E.D.T.A.
Bring pH to 10 with 1N NaOH (exact volume added)

Rinse Solution

100 ml rinse solution (exact volume)
Bring pH to 10 with 1N NaOH (exact volume added)

Treated Process Solution (Two cases)

1) 10 ml of centrifuged sample free of solids if pH below 10
   10 ml distilled water (exact volumes are ncessary)
   10 ml 0.1M disodium E.D.T.A.
   Bring pH to 10 with 1N or .5N NaOH

2) 10 ml of centrifuged sample relatively free of solids at pH above 10.
   10 ml distilled water. (exact volumes are necessary)
   Bring pH to 10 with 0.5N HCL

Approximately 100 ml of the following standards are necessary for analysis:

NaF concentration (moles/liter)	Resulting Single Fluoride Ion Activity at 25°C. (moles/liter)
10^{-1}	0.77×10^{-1}
10^{-2}	0.91×10^{-2}
10^{-3}	0.97×10^{-3}
10^{-4}	10^{-4}
10^{-5}	10^{-5}
10^{-6}	10^{-6}

Expanded-Scale pH meter and Specific Ion Electrode. An expanded-scale pH meter similar to the Beckman Expandomatic SS-2 is used in conjunction with the Orion Research Fluoride Electrode.

Analysis Procedure

1) Standardize the expanded scale of the meter for a range of ±200mv

2) Measure the millivolt potential of the six sodium fluoride standards employing the specific ion electrode

(Cont'd)

3) Prepare a process, rinse, or treated process sample

4) Measure the millivolt potential of the sample; accept a reading which stabilizes for at least 5 minutes

5) Measure the Specific Conductance or "Conductivity" of the sample in micromho/cm

Calculations

Conductivity (Micromho/cm.)	Ionic Strength (Moles/Liter)
10	1.1×10^{-4}
50	5.7×10^{-4}
100	1.2×10^{-3}
500	6.2×10^{-3}
1000	1.3×10^{-2}
5000	7.1×10^{-2}

Construct a series of plots of Conductivity vs. Ionic Strength on log-log paper per the example shown in Figure 2

6) Determine total ionic strength of sample from above plot

7) From curve of ionic activity coefficient as a function of total ionic strength determine activity coefficient of fluoride ion (see Figure 23)

8) Calculate fluoride concentration using following equation:

$$\text{ppm Fluoride} = \frac{(MV_A - M_s)(A_B - A_A)(D_L)(19 \times 10^3)}{(MV_A - MV_B)(\gamma)}$$

where:

M_s - Expanded scale millivolt reading of sample

MV_A - Expanded scale millivolt reading of sudium fluoride standard having a higher millivolt potential than sample

MV_B - Expanded scale millivolt reading of sodium fluoride standard having a lower millivolt potential than sample

A_A - Activity of standard A, moles/liter

A_B - Activity of standard B, moles/liter

D_L - Dilution ratio $= \dfrac{\text{volume of undiluted sample + volumes added for sample mixture}}{\text{volume of undiluted sample}}$

γ - Activity coefficient of fluoride ion from (7) above

19×10^3 - factor for converting fluoride concentration from moles/liter to parts per million

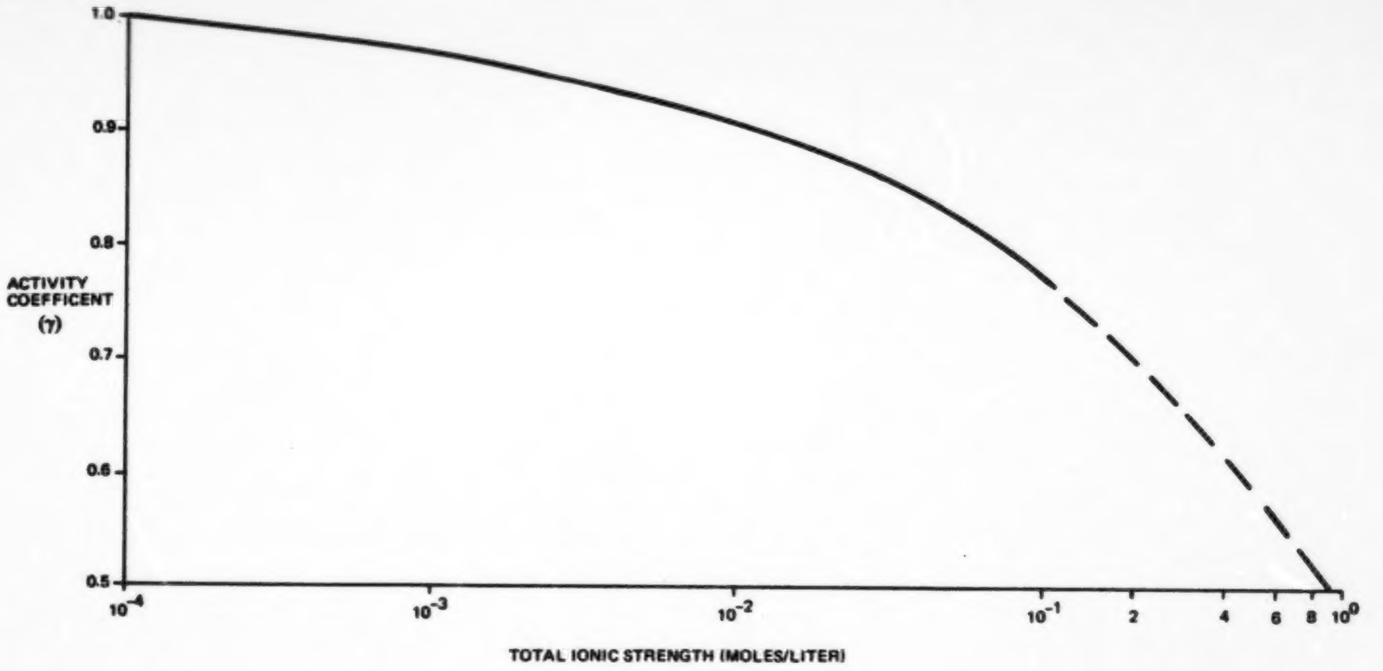

Figure 23. Ionic Activity Coefficient of Fluoride Ion as a Function of Total Ionic Strength